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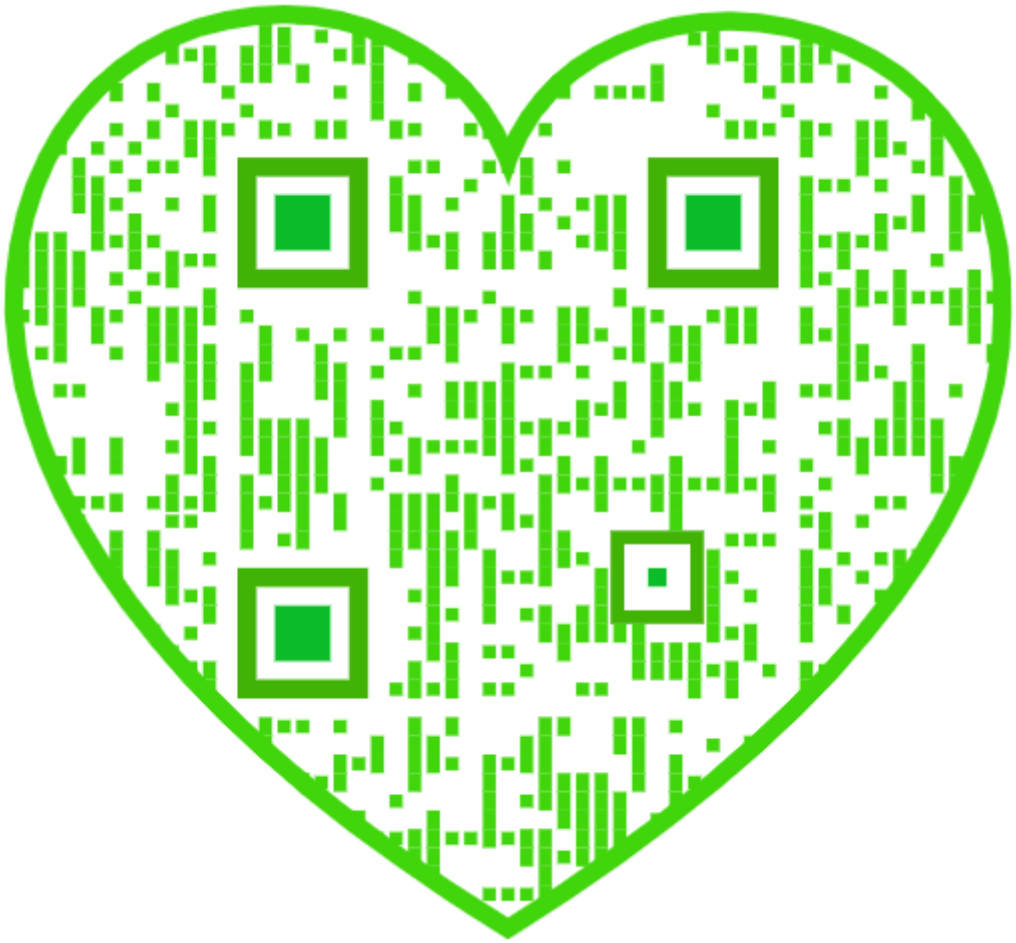
THE CHEMICAL INDUSTRIES



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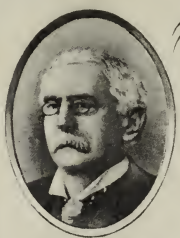

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INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

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RUBBER, RESINS, PAINTS AND VARNISHES

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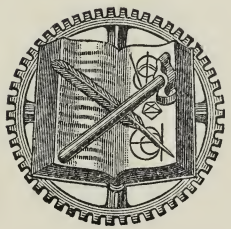

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GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from

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the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental

munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHORS' PREFACE

It has been our endeavour to present to the advanced student a brief summary of the properties of paints and varnishes together with those of their components, and a general statement of the principles underlying their manufacture. It is of importance to lay stress on the urgent need for research in the domain of oils and resins, not only on their chemical properties and composition but on those properties due to surface action and catalysis. Many properties of solutions of suspensoids and emulsoids are presented in varnishes and paints which are only recently receiving systematic investigation. Paints and varnishes have long been considered solely from the craftsman's standpoint. Progress has been uneven, and from the methods of investigation employed the industry is wrapped in a thick cloak of trade secrets.

In the description of the manufacture of varnishes and paints care has been taken to avoid technical details beyond what are required to illustrate general principles. In dealing with paints the essential requirements are set forth without burdening the student with details of formulæ which are often untrustworthy. We have attempted to treat the subject in the spirit of the Editor's General Preface and are indebted to him for the section on the Rubber Hydrocarbons.

A section on the linoleum industry has been included, for the reason that linoleum, paints and varnishes, have much in common from the standpoint of the general properties of drying oils.

We desire to express our thanks to Messrs. Mander Brothers, Wolverhampton, and to Mr. D. Gestetner of the Neo-Cyclostyle Works, Tottenham Hale, London, for permission to collaborate in the writing of this book.

We are glad to acknowledge the assistance given by Messrs. Constable & Co., Ltd., Messrs. Manlove, Alliott & Co., Messrs. Rose, Down and Thompson, and Messrs. Torrance & Sons, Ltd., in the representation of plant used in the industries.

Our thanks are also due to Mr. P. J. Fay, M.A., for reading the proof sheets while the work was passing through the press.

R. S. M.
A. de W.

WOLVERHAMPTON AND LONDON.
December, 1920.

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(INDIARUBBER: CAOUTCHOUC).

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RUBBER, RESINS, PAINTS AND VARNISHES

Part I.—THE RUBBER HYDROCARBONS

(Indiarubber : Caoutchouc)

The British rubber plantation industry has reached its present position more by luck and enterprise than systematic cultivation trials : and, as in many other industries, the initial success was brought about without much scientific thought. By this, we do not mean that the pioneer work of men like Hancock, who suggested cultivating rubber in the East and West Indies early in the last century, Collins in Singapore sixty years ago, and the later success of Wickham in Ceylon with *Hevea Braziliensis*, have not more than justified the boldness with which these earlier enterprises were marked. It is rather to express surprise that so much has been done at our botanical experimental stations by men like Ridley at Singapore, and the Indian Government at Heneratgoda and Peradeniya in Ceylon, with the small amount of scientific assistance and monetary help placed at the disposal of planters in these two typical British tropical centres.

Nearly all the effort of the last thirty years has been directed to the trial and selection of native and wild rubbers in different climates and soils rather than any attempt at botanical experimental cultivation for producing new varieties with increased yield of latex or greater resisting power to infectious disease. Nothing comparable to the Canadian improvement in wheats or the phenomenal development in the cultivation of the sugar beet on the

Continent has at present been achieved in the case of cultivated rubber. The transplantation and cultivation of the cinchona in relation to the yield of quinine shows the possibilities in this direction.

Seeds from Hevea trees, derived from Malay, which have sprung up from the parent stock in Ceylon, have now been grown in almost all known likely rubber-producing areas in the tropical world, so that data are now available for a careful study of the conditions which contribute to economic growth. The Cicely estate at Teluk Anson has sent seeds and cuttings to both East and West Africa and to districts so far remote as Fiji and Queensland, and it would seem probable that the older plantations of Ceara on the East and Funtumia on the West coast of Africa will give place to the Hevea variety, and that consequently the breeding of this rubber will probably ensure its survival as the fittest for industrial growth.

For improving the yield, and at the same time ensuring a robust and long-lived tree, the necessity for long period trials from selected seeds is essential; development of our knowledge must necessarily be slower than in the case of annuals like wheat or sugar beet. Our present supremacy in this plantation industry must not be allowed to decay through any neglect of studies in this direction. It must not, however, be forgotten that whilst our British plantations may be maintained in the way indicated, the problem is not only one of industrial botany, but depends on the suitability of the product for the markets of the world, and here we depart from the botanical cultivation of the plant to the chemical and physical properties of the latex, and the methods adopted for its coagulation and ultimate vulcanization by the home user.

To correlate these several factors is no easy task; and the Rubber Growers' Association and the laboratories here and in the East have long investigations in front of them, and it is doubtful if the planter, relying on the information to be obtained from botanical experimental cultivation, will succeed in improving his position, unless the subsequent

fate of his product is known. There is at the present time considerable lack of knowledge as to the causes of the variability of plantation Para rubber with different technical mixings, so that until we know what are the conditions of growth which cause the latex to have a different rate of cure when coagulated, further progress in this direction must be slow.

At Kuala Lumpur, the Department of Agriculture of the Federated Malay States has done good work in this direction during the last few years by obtaining evidence which goes to show that the latex contains, in addition to the rubber, proteid substances which modify the rate of cure, and that these substances are not precipitated by ordinary coagulation.

To obtain uniformity in first latex rubbers, the nature of this proteid, its amount, and in fact all the conditions of its formation in relation to the latex production, must be ascertained before further progress in standardization can be effected.

Buyers know that an over-smoked rubber has lost much of its value, and planters seldom now err in this direction. Besides over-smoking, over-washing and over-machining and the excessive use of sulphite and preservatives contribute to the destruction, or prevent the formation of the catalytic proteids which seem so essential for rubber to behave well on vulcanization.

As a matter of fact, the Kuala Lumpur Agricultural Station is now engaged on the study of these problems, and useful experimental work is being done in the East, and at Delft, in Holland, under the Dutch Government; but there is need for comparison of the work and correlation of the results obtained at these different centres of investigation with the Ceylon research and that which is going on in Africa, more especially at Aburi.

It is only quite recently that Whitby has again made a comparison of the Brazilian and plantation methods of preparing Para rubber, and from the results of his investigations it seems clear that the Brazilian method of preparing

rubber by smoke coagulation is not superior to the plantation method of preparing it as smoked sheet. He also shows that the latex from young trees is not inferior to that from old trees, in fact, the rubber prepared from the latex of young trees proved superior to that from the latex of old trees, both when prepared as smoked sheet and when prepared by smoke coagulation in the Brazilian fashion.

The experimental botanical stations of our plantations in the tropics cannot also afford to ignore the work of the English and German chemists on the synthetic production of rubber. Synthetic rubber exists, and was probably of use to a limited extent during the war, just as synthetic nitrates exist and have rendered the war possible, although we still look to the tropics for both these materials.

The chemist can demonstrate the conversion of starch into isoprene or butadiene, and Harries is confident that the rubber obtained from isoprene with the aid of acetic acid in the laboratory is identical with that coagulated from the plant latex by the same acid in the field. The botanist has yet to tell us how in Brazil, or in Malay, the plant converts its starch into the isoprene polymer.

It may be held that the natural rubber is elaborated from cellulose itself and that starch is not the elemental source of the rubber latex. Sawdust under pressure can be hydrolysed to lævulinic acid, and this substance has in the laboratory, by the aid of phosphorus trisulphide, been first converted into methyl thiophene which loses its sulphur when heated with copper in a stream of hydrogen and forms isoprene. Although the plant brings about these changes in an unknown way, it certainly accomplishes the task in a more economic manner; so that, at the present time, the natural product takes the field and gives us another example of the advantages which nature has over the products of the laboratory when accurate knowledge of scientific agriculture is brought to bear upon tropical plant development.

The Raw Materials: their Formation in Nature, their Distribution

It is difficult to give a scientific definition of rubber. An elementary chemical analysis shows that it has the empirical formula C_5H_8; that is, identical with that of the large class of naturally-occurring substances known as terpenes. This does not, however, represent the molecular composition, and as far as the naturally occurring rubber is concerned this has not yet been definitely determined. The main reason for this is that rubber is a colloid.

By destructive distillation of coagulated rubber, simple hydrocarbons of definite and known composition have been obtained, and it is probable that the rubber molecule is a condensed or polymerized form of these hydrocarbons. Our knowledge on this point, however, is still very obscure and therefore uncertain and contradictory.

The subject is further dealt with under synthetic rubber.

Origin and Distribution.—The material commonly known as rubber does not occur naturally as such, but is obtained from a fluid known as latex which is secreted by many plants—the so-called rubber plants. The fluid flows out of the plant when the latter is wounded or tapped, and by the addition of acids and heat it becomes coagulated and forms what we recognize as rubber. From an economical point of view the formation of the latex in the plant, its distribution and its function is of the greatest importance and will therefore be briefly dealt with here.

The latex is contained in the cellular tissue just outside the ring of cambium and is distributed in that portion of the plant by the so-called laticiferous vessels. These form a complex anastomosing network, better seen when a longitudinal section is cut. The cambium layer, which is adjacent to the laticiferous-bearing tissue, is the most important part of the plant, as growth within and without takes place from this layer. If, therefore, on tapping a

rubber tree the cambium is damaged by too deep a cut, irreparable damage is made to the plant. Any form of tapping must therefore avoid the cambium, and preferably should aim at getting latex from only a portion of the laticiferous vessel in order that the function which the vessels play in the life of the plant may be interfered with as little as possible. Up-to-date tapping methods recognize this and various instruments are in the market which more or less meet with these requirements.

Like the fluids in all plants, the latex is primarily formed from carbon dioxide and moisture by the influence of sunlight, heat, enzymes and catalytic agents, and various hypotheses have been put forward to explain how the rubber hydrocarbons are synthetized by the plant.

Experiment has shown that the green colouring matter present in the leaves of plants is the active agent in the decomposition of carbon dioxide and that the change cannot be brought about by the colourless protoplasm. The preliminary stage is accompanied by the liberation of oxygen, and formation of formaldehyde—

$$CO_2+H_2O=O_2+HCHO$$

The reaction does not proceed so simply, and hydrogen peroxide, together with other oxidases like percarbonic acid, are no doubt also produced, thus, according to Bach—

$$3H_2O+3CO_2=2(H_2CO_4)+HCHO$$
$$2H_2CO_4=2CO_2+2H_2O_2$$
$$=2CO_2+2H_2O+O_2$$

All the products have been identified in various plants.

The work of Butlerow and others has, however, shown that formaldehyde is converted into carbohydrates—notably fructose; and the presence of sugary substances in most rubber serums at once suggests the possibility of rubber being derived from a sugar.

Now, erythritol, a direct sugar derivative, is easily converted by the action of formic acid into erythrene or butadiene from the methyl derivative of which synthetic rubbers,

very similar in character to natural rubbers, have been obtained in the laboratory—

$$CH_2OH-CHOH-CHOH-CH_2OH \rightarrow CH_2=CH-CH=CH_2$$

Further, according to Harries, when rubber is oxidized by means of oxygen or ozone, lævulinic aldehyde is formed, and this is identical with the product formed when carbohydrates such as starch are treated with acids. This aldehyde contains the C_5H_8 grouping.

Function of Latex in the Plant.—The exact function which latex plays in the life of the plant is not known, and several views, all more or less contradictory, have been put forward to explain the work which the latex is called upon to perform. The solution of the problem is very important from the practical standpoint, for if the latex is considered to be a waste product of the plant its entire removal would be without injury to the plant. On the other hand, if the latex has an important functional purpose to fulfil, then tapping operations in the plant must be carefully performed in order not to drain the plant and thus imperil its existence.

The most recent and extensive investigations have been carried out by Vernet, who has studied the subject very thoroughly, and he arrives at certain definite conclusions. His views and experiments are briefly put out as follows :—

Is the latex an excretory product? "Plant secretions are usually products which the plant diverts into large cavities, where they remain imprisoned during the whole life of the plant out of all contact with other liquid food materials.

"Latex vessels, however, are far from being closed vessels. They form a continuous network in which the meshes are all inter-connected. Further, the quantity of latex varies very considerably at different times, and this is a most unusual occurrence if the latex be regarded as an excretionary product."

If the latex were an excretion, then it could be removed

without causing injury to the plant. To answer this question Vernet completely severed the latex vessels from a Hevea tree and found that it entirely lost its leaves and therefore suffered from the treatment. The latex cannot therefore be an excretion whose presence is immaterial to the plant.

Having thus shown that latex is not an excretion Vernet definitely asserts that the latex as a whole is a food indispensable to the life of the tree, and confirms his evidence by analogy, chemical composition and effects of tapping.

Analogy.—The laticiferous vessels are morphologically very similar to sieve tubes which are the recognized organs for nutrition and circulation in all plants. The vessels are more numerous near the generative or cambium layer, just where one would expect the nutritive function to be most necessary, and are found in all stages of the plant's existence, even in the embryo of the seed and the young germinating plant.

Chemical Composition.—The latex besides containing water and rubber contains also sugars and proteins, *i.e.* materials indispensable to the nutrition of plants.

Tapping.—The rate of increase in girth of a tree which follows upon tapping is less than normal, but becomes more than normal when tapping ceases. The seeds also lose in weight after tapping. All the above facts go to show that the formation of latex is a continuous function of a plant's life-history. The flow is not continuous, and after tapping naturally slackens down, thus promoting coagulation of what is left on the wounds and so stopping the process of bleeding. The latex thus serves a protective function in addition to that of nutrition.

Rubber-bearing Species.—The number of plants which yield a rubber containing latex is very great and belongs to four natural orders—Euphorbiaceæ, Artocarpeæ, Apocynaceæ and Asclepiadeæ. The plants vary considerably in size ; some are herbaceous and contain latex in their roots or stems, while others are climbers or vines and

yield latex from the branches. Others, again, are shrubs; but the bulk from which the rubber of commerce is obtained are forest trees of considerable size.

The tree which gives the best rubber is *Hevea Braziliensis*, which grows wild in the basin of the Amazon, Brazil. The tree is the most important of the order Euphorbiaceæ, grows to a height of 50 to 65 feet, and the trunk attains a diameter of 60 to 70 inches. Rubber was first discovered from this tree, and the method of tapping and coagulating the latex has remained unchanged even up to the present day in its native habitat. The tapping consists in forming an incision on the tree about 6 feet from the ground and collecting into cups the latex which immediately oozes out. This is then poured in a thin stream on the flat part of a paddle, which is rotated on a smoky fire. In this way the latex coagulates at once, and forms a layer on the paddle, and when by continual rolling and pouring of latex the layers reach a weight of, say, 20 lbs. the rubber is branded and sold as "Fine Para." This still obtains the best price. The number of Hevea trees in the Amazon valley is estimated at 200 million, of which a half are being tapped. Other species from which rubber is obtained are—Castilloa and Manihot trees and Guayule shrubs, all in South and Central America, where the method of collection and coagulation is practically the same in all these cases.

In Africa the rubber-yielding plants belong mainly to the order Apocynaceæ, and include trees like Funtumia as well as shrubs, creepers and plants with rhizomes. Each of these species of plant requires its own method of treatment for the winning of the rubber latex, but all the methods are unfortunately crude and have been adopted with no eye for the future either of the plant or the Rubber industry.

The rubber from the herbaceous plants is obtained by drying the roots in the sun, cutting them into small pieces and chipping off the bark by striking with a mallet. The pieces of bark are next treated in the same manner and the latex which issues from the tissues allowed to dry into

masses. These are cut up, purified by putting into several changes of boiling water, and then massed into sheets. In the case of creepers, the stems are cut into pieces and the latex which exudes from the cut ends collected in a hole dug in the ground.

In Asia the natural rubber plants differ entirely from those in America and Africa in that they yield very resinous rubbers. In fact, very few rubber trees may be said to exist here, although climate and soil appear quite appropriate to the Hevea type of plant. This being so, attempts were made some thirty or forty years ago to cultivate the ordinary rubber plants in this portion of the globe. *Hevea Braziliensis* being the plant which yields the best rubber, was chosen as the best type of plant to introduce, and extensive plantations were laid down. Many difficulties were encountered, one very important one being that the seeds quickly lost their germinating power and had therefore to be planted and allowed to germinate during the voyage. The trees also do not give a profitable yield of rubber till they are more than five years old, so that the risk attending failure was great. The yields, however, increase as the plants grow older and may reach $3\frac{1}{2}$ to $4\frac{1}{2}$ lbs. per annum. Attempts have also been made to cultivate *Manihot Glazovii* as this lends itself to an easy method of cultivation, but although the rubber obtained from it is good, the yield is poor, not exceeding 18 ozs. per annum. In spite of preliminary setbacks the plantations have been a great success and many millions of capital have been sunk in them. The number of Hevea plantation trees was estimated at 60 millions some years ago, and the weight of rubber produced in 1911, 14,000 tons as compared with 38,000 tons from the Amazon; but in 1919 some 320,000 tons of rubber was the actual world's consumption, showing the very rapid development in the plantation industry within the last decade. The United States shows an average annual increase of 27·7 per cent. during this period. The output from Brazil has fluctuated from 42,000 to 26,750 tons per annum, and wild rubber has not exceeded 30,000 tons per annum.

The following table shows the rate of increase in the world's rubber production during the last three years :—

	From plantations (long tons).	Other sources (long tons).	Total (long tons).	Average price per lb. in London.
1916	152,650	48,948	201,598	2*s.* 9¾*d.*
1917	213,070	52,628	265,698	2*s.* 9¾*d.*
1918	200,950	40,629	241,579	2*s.* 3½*d.*

and this shows at once the growing importance of plantation rubber in the world's market.

The plantation in Malaya alone produced 177,000 tons in 1919, while the Netherlands Indies produced some 76,000 tons. The area under plantation is estimated at 2,760,000 acres of which only 2,000,000 are of bearing age. In 1920 the consumption is estimated at 350,000 tons, with an over-production of 34,000 tons, and with a steady increase in plantation output it is anticipated that the figure for 1924 will be 640,000 tons.

By far the greatest consumer of the world's rubber is the United States, and the following table shows that nearly three-fourths of the world's production is manufactured in that country. Great Britain, which virtually commands all the plantation areas, comes second, using only one-tenth of the world's supply.

Consumer.	Population.	Rubber consumed (tons).	Per cent.	Productive value. £
United States ..	92,000,000	177,088	69·0	177,000,000
Great Britain ..	45,000,000	25,983	10·2	26,000,000
France	40,000,000	17,000	6·7	17,000,000
Italy	35,000,000	9,000	3·5	9,000,000
Russia	174,000,000	7,500	3·0	7,000,000
Canada	7,000,000	6,287	2·7	6,300,000
Scandinavia	—	5,323	1·9	4,500,000
Japan and Australia ..	—	4,500	1·8	3,000,000
Germany and Austria	117,000,000	3,000	1·2	—

Tapping

The methods for tapping the rubber have undergone considerable changes during the ten years in which systematic production in the East has been conducted. Daily tapping was felt to be too great a strain upon the tree, and thus many estates adopted tapping on alternate days, and on some a three-day period was adopted. The number of cuts per day were also altered until most estates, attracted by the good yields, considered that two superimposed cuts on one-quarter of the tree were not too much, but lately, owing to the war and a desire to restrict production, one cut per day on one-quarter has come more into vogue. There is no doubt that a conservative method of daily tapping will prolong the available life of the tree and give ample time for bark renewal. The cuts should be sufficiently close to take up not more than an inch of bark per 22 cuts.

Physical and Chemical Properties of Latex

Physical Properties.—The latex of a rubber tree is a white or pale yellow milky liquid, varying in consistency according to the rubber it contains. It stains the hands black, develops an odour of methylamine on standing and has an alkaline reaction. Its specific gravity ranges from ·905 to 1·041, the average being about 1·018, corresponding to a rubber content of about 32 per cent. Speaking generally, the lower the specific gravity the greater the percentage of rubber, and tables have been drawn up from which the rubber content is obtained directly by referring to the gravity at a definite temperature. The "metrolax" gives the percentage of rubber in the latex as shown by its gravity.

The rubber in the latex exists in the form of nearly spherical globules, having an average diameter of one-thousandth of a millimetre, and when observed under the high power of a microscope exhibit the well-known Brownian

movement. The movement is very irregular, and cinematograph films show that the path traced out by each particle is a long one. The effect of the addition of chemicals has been studied. Soda has but little effect on it. Acetic acid completely holds up the movement even before coagulation sets in. A 20 per cent. solution of sodium chloride arrests the movement completely, and the number of particles counted under these conditions amounts to 50 million per cubic millimetre. Salt has been used as a coagulant in East Africa.

Direct experiment has shown that the rubber content of latex varies with the height from which the tree is tapped, and also with the age of the tree. Thus from a Ficus plant 7 ft. 4½ ins. high Adriani found—

At 12 ins.	latex contained	25	per cent.	rubber	
,, 5 ft. 6 ins.	,,	,,	24	,,	,,
,, 6 ft. 10 ins.	,,	,,	20	,,	,,
,, the top	,,	,,	17	,,	,,

At 6 years	the latex of a Castilloa tree contains				20 %	rubber
,, 7	,,	,,	,,	,,	27 %	,,
,, 8	,,	,,	,,	,,	29 %	,,
,, 9	,,	,,	,,	,,	31 %	,,

Chemical Properties.—An average chemical composition of the latex of a full-grown Hevea tree shows that it contains—

Water	55·0
Rubber	41·0
Sugars	·8
Albuminoids	2·8
Mineral Matter ..	·4
	100·0

In addition, small quantities of oxidases, resins and sulphates are present. On standing, coagulation takes place, and the rubber separates as a colloid and leaves a clear serum. Hevea latex is alkaline in reaction as it issues from the tree, but becomes acid after a little time, owing

probably to fermentation of the sugars present. The latex becomes acid in very much the same way as milk sours, and coagulation then takes place under the influence of the acid formed. Most other latices are, however, acid as tapped.

Latex can be kept without alteration for about twelve hours. Beyond this, watering or the addition of chemicals is necessary to prevent chemical change taking place.

Concentrated acetic acid, formic acid, citric acid, and other strong organic acids bring about coagulation very rapidly. The globules join up, forming chains similar to streptococci; they swell to twice their volume and then separate out together as a coagulum.

Acetic acid is the usual coagulant employed in plantation areas, but citric and formic acids are also used. Hydrochloric acid is a very powerful coagulant, a current of gas producing coagulation almost at once, and rubbers which are inclined to be tacky lose this tendency by this treatment. If the treatment is prolonged chemical action proceeds further. The rubber hardens and turns to a mass resembling ebonite. Carbon dioxide is also an excellent coagulant and no doubt is the active agent in the out-of-date smoke coagulation still carried out in the Amazon.

The threatened shortage of acetic acid in the plantations has caused attention to be given to natural or spontaneous coagulation, and the method introduced by Maude and Cross —the so-called M.C.T. process—in which separation of rubber from latex is allowed to take place under the anaerobic conditions produced by the carbon dioxide, has been commented on very favourably, and is said to yield a rubber which in its degree of uniformity is superior to any other form of plantation rubber.

Sodium chloride, mercuric chloride and phenol precipitate rubber from its latex and all protein precipitants behave towards latex as coagulants. Formaldehyde, very curiously, has little action even when heated. The author suggested acid sulphate of soda as a coagulant during the war.

The carbohydrates and glucosides which occur in the serum of rubber latex have received a great deal of attention,

and the presence of the C_5H_8 group, or multiples of it, which has been definitely established in them, points to the fact that rubber is very probably elaborated by the plant from these sugars.

The work of Aimé Girard in this connection is worthy of mention. Working with the serum of fresh latices he obtained coloured masses after evaporation, and these on extraction with alcohol produced white colourless crystals which he called Dambonite. This compound has the empirical formula $C_4H_8O_8$, melts at 190° C. and volatilizes at about 210°, forming long needles. It does not reduce Fehling's solution nor undergo alcoholic or lactic fermentation. It is attacked by strong acids (HI) with the formation of methyl iodide and a neutral substance having a sweet taste, a fine crystalline structure and the composition of a dehydrated glucose. This substance he called Dambose.

Similar sugars were obtained from the latices of other rubber plants, and lastly, in 1911, Pickles and Whitfield succeeded in proving the presence of dambonite in Hevea latex.

The presence of sugars in the latices of all rubbers thus strengthens the belief that rubber is a sugar derivative.

The mineral salts in rubber latex are very small in amount and have the normal composition, K, Ca, Mg, and Na salts having been identified. Oxalates have also been found. Acidity is usually very small. The resins present are separated by extraction with alcohol or acetone, but very little is known about them. They are optically active and are precipitated with rubber on coagulation. In some plants the percentage of resin is greater than that of rubber, and their extraction from the latex before instead of after coagulation would produce a better quality rubber.

All latices examined have shown the presence of proteins, and these differ from ordinary proteins in being very slowly and incompletely precipitated when heated. The proteins behave normally with all alkaloidal precipitants and protein coagulants, and experiment has shown that coagulation of latex is really a coagulation of proteins and not of rubber

itself. This question, in fact, involves that of the presence of rubber as such in the latex, and Preyer, Weber, and others have shown that rubber separated from latex by a centrifuge is not precipitated by coagulants. Further, the addition of ether to latex does not extract a solid hydrocarbon, but on evaporation of the ether a thick oil is first obtained which only after some time solidifies to pure rubber.

The coagulated latex after washing is marketed in the form of crepe or smoked sheet. Bisulphite of soda is usually added to produce a pale coloured crepe. Various devices are used for recovering the scrap rubber adhering to the trees, which appears on the market as bark scrap and "compo."

The drying and smoking of the sheets have to be carefully attended to so as to ensure uniformity and freedom from spots or discoloration, which detract from the value of the finished sheet.

Chemical and Physical Properties and Testing of Rubber

Chemical Properties and Composition.—Before examining the chemical properties, the purity of the rubber must be established. Resins, protein, etc., must be removed, and when this is done the question still remains as to whether the product obtained is a simple substance. Unfortunately, rubber has no definite melting point, neither have any of its derivatives with the possible exception of the ozonides obtained by Harries.

Neglecting these preliminary handicaps and proceeding as with other organic substances one finds that carbon and hydrogen are alone present, and that the empirical formula corresponds with C_5H_8. The molecular weight has not been determined with certainty, as, like all colloid substances, it has no osmotic pressure in solution, and freezing-point and boiling-point methods are useless. The rubber molecule is no doubt a large one, and its formation is due to the union of nuclei of 5 to 10 carbon atoms. According to Bary and

Weidert vulcanization is the addition of one atom of sulphur at each end of a chain of $C_{10}H_{16}$ nuclei; thus $(C_{10}H_{16})_nS_2$; and as 2·5 per cent. is the amount of sulphur required to bring this about, it follows that the figure for $(C_{10}H_{16})_n$ must correspond to about 2500. This, however, does not agree with the molecular weight of two derivatives—the ozonide and the nitrosite, which contain 10 and 20 carbon atoms respectively, and as there is no reason why the parent substance should contain any more, it is very probable that this also contains the same number of carbon atoms.

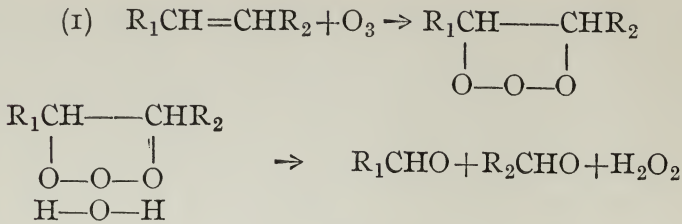
The rubber molecule is thus an unsaturated hydrocarbon, but the most satisfactory proof of the presence of unsaturated linkages is obtained from the work of Harries, who applied his method of ozonization previously used to settle the formulæ of oleic acid and other unsaturated compounds. When ozone is passed into a chloroform solution of pure rubber an explosive oil is obtained which solidifies in vacuo and melts at 50° C., and the molecular weight of this compound corresponds to $C_{10}H_{16}O_6$. But previous investigations have shown that each three atoms of oxygen are attached to one double bond, hence there can only be two such linkages for every ten carbon atoms. More recent work has shown that rubber in a similar manner gives a diozonide.

Having established the presence of two double bonds, Harries set about to determine their position in the molecule. This he did by hydrolysing the ozonide with steam and examining the product obtained. By this means he was able to show that the ozonide on hydrolysis produced hydrogen peroxide and lævulinic aldehyde, and the latter then oxidizes to lævulinic acid. Thus—

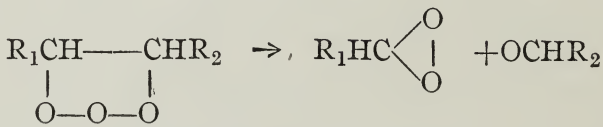
$$C_{10}H_{16}O_6 + H_2O = 2(\underset{\text{Aldehyde.}}{CH_3.CO.CH_2.CH_2.CHO}) + H_2O_2$$

$$CH_3.CO.(CH_2)_2.CHO + H_2O_2 \rightarrow \underset{\text{Acid.}}{CH_3.CO.(CH_2)_2.COOH} + H_2O$$

The changes take place at the double linkage, thus—



Under certain circumstances peroxides may be formed, thus—

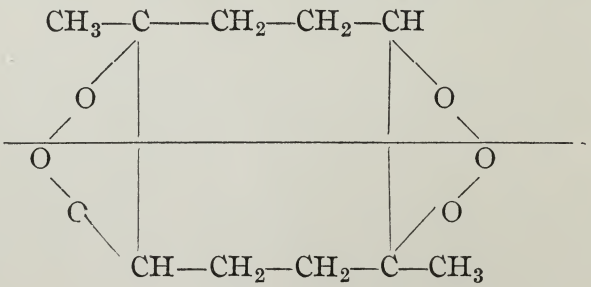


From the ozonide we may therefore obtain—

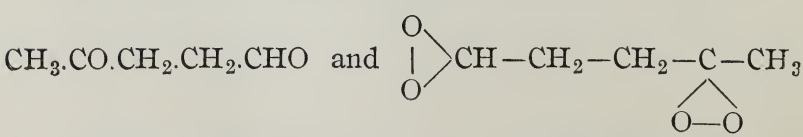
Lævulinic Aldehyde.
Lævulinic Peroxide.
Lævulinic Acid.

To explain these reactions one must regard the ozonide molecule as a cyclic one, for if it were a chain molecule, the diozonide would give two hydrolysis products oxygenated at only one end of their chains as shown above, (1).

The formula which explains all these reactions is—

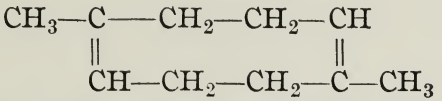


By the influence of steam this splits up as shown into



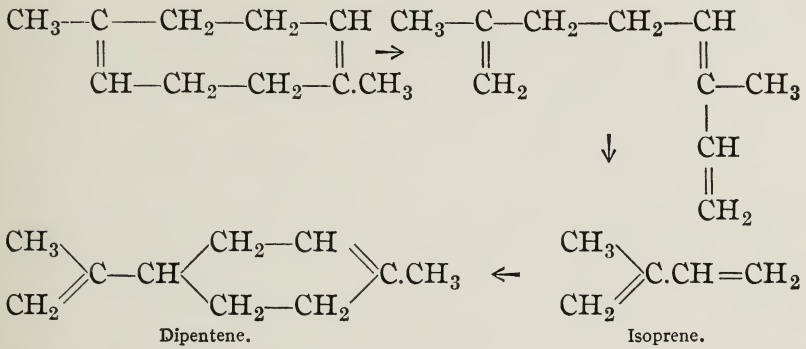
Lævulinic aldehyde. Lævulinic peroxide.

It follows, therefore, that the original hydrocarbon must have the formula—

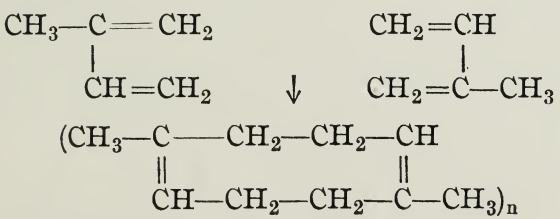


i.e. 1·5 dimethyl cyclo-octadiene 1·5.

This formula further explains the formation of isoprene and dipentene, which are obtained on distillation thus—



But isoprene can be polymerized to a product very similar to rubber thus—



Hence the definite decomposition products and derivatives can be explained by the formula, and this must therefore be taken as the correct one for the time being.

Testing of Rubber.—A chemical analysis of rubber is seldom necessary, but is required when mechanical tests do not give normal figures.

The *moisture* is determined by drying at a temperature of 90° to 100° F. *Resins* are extracted with acetone, the acetone evaporated and the resins dried and weighed. *Proteins* are determined by multiplying the nitrogen content

as obtained by the ordinary Kjeldahl process by 6·25. Matters insoluble in benzene or some other solvent are determined and considered separately, even though they contain proteins. Mineral matter is determined by decomposing and burning by means of heat. The sum of these impurities as percentage subtracted from 100 gives the rubber as a difference figure.

Some chemists, however, prefer to determine the rubber or caoutchouc by estimating the amount that passes into solution. The tests on which one bases the price and therefore the quality of the rubber are, however, all mechanical tests, and in recent years a great number, based on new principles, have been suggested and in some cases adopted.

Unfortunately, the method most commonly practised consists in nothing more than smelling, seeing if it tears when stretched between two hands or gives way to a strong push of the finger and thumb. Thus more definite and reliable methods have for a long time been wanted.

For plantation areas the following tests have been suggested :—

1. Viscosity of rubber solutions of definite strength.

2. *Adhesion tests.* A solution of rubber is brushed on a piece of cloth or strong paper and allowed to dry. The dry sheet is next folded and the two surfaces pressed together and made to adhere. The weight required to tear the adhering surfaces is then determined.

3. *Tensile strength.* Rubber is pressed into a definite shape during cooling or drying and the elongation produced by loading weights on one end obtained.

From the manufacturers' point of view, the tests must be somewhat modified in order to meet the various uses to which the rubber is to be put.

The most favourite is the tensile test which determines the breaking stress per unit of cross-sectional area and the elongation at rupture. The elongation under constant load and the effect of varying the load below the limit of breaking stress are also determined. All these tests lay bare the mechanical strength of rubber.

To get an idea of the resiliency of rubber a different series of tests has to be performed, and these tests determine the "Permanent set" or coefficient of resiliency and "Sub-permanent set." The permanent set is the permanent increase in length after the full retraction which follows the withdrawal of a stress. If this is measured at definite intervals before the rubber has had time to fully retreat we then get the sub-permanent set. When the elongation obtained by gradually increasing loads and the retraction by gradually decreasing the loads are plotted, an hysteresis curve is obtained and the form of a series of such curves is probably the best indication of the quality of the rubber.

Manufacture of Rubber Articles

Before the rubber can be used for manufacturing purposes it must undergo such treatment as will remove any impurities present and bring it to a form suitable for the particular article required to be made from it.

The removal of impurities, which usually consist of more or less foreign matter, such as sand, dirt, bark and moisture, is carried out by the process known as "washing." For this purpose the raw rubber is cut into lumps or slabs, steeped in warm water to render it pliable and remove some of the soluble impurities, and then passed through corrugated rollers. A stream of water is kept running on the rubber throughout the operation. By the continued squeezing and disintegrating action of the rollers, the original lumps or slabs of rubber are converted into thin corrugated sheets, and the process is stopped when the rubber is considered thin and clean enough. The sheets are next dried on racks in a drying chamber until the moisture content is 0·25–0·5 per cent. The drying chambers are steam-heated, but the cooler and drier the atmosphere is, the better is the product obtained; otherwise the rubber is inclined to become "tacky." The normal drying temperature is 80° F. and the drying takes three to four days, if ventilation conditions are suitable.

When dry and clean the rubber is made to undergo the process of *Mastication,* by which means it is converted into a soft doughy mass. The process is carried out by repeatedly passing the rubber between smooth, hollow; steam-heated rollers. After about half an hour's treatment, the rubber is usually of the required consistency and ready for the next process—*Mixing.* Here the rubber is incorporated with the various other constituents which are considered necessary for the production of the final article. Very few articles are made with rubber alone, partly on account of its price, and partly owing to its excessive softness and elasticity, so that the mixing process is one which must be carried out with practically every kind of rubber article manufactured. The materials other than rubber and sulphur which are employed in commercial mixings may be classified as follows :—

(*a*) "*Cheapeners.*" These include such substances as powdered chalk, barytes, ground rubber waste, zinc oxide, etc., and are added for no other purpose than to cheapen the final article.

(*b*) *Materials added for a definite purpose,* such as (1) to increase mechanical strength, *i.e.* toughen or harden the goods—*e.g.* zinc oxide, magnesia (oxide and carbonate), lime and litharge. (2) To improve vulcanizing conditions, *e.g.* litharge, magnesia, quicklime, antimony pentasulphide or any other polysulphide. (3) Colouring matter, *e.g.* zinc oxide, zinc sulphide, antimony sulphide (golden and crimson), mercury sulphide (vermilion), cadmium yellow, chrome yellow, chrome green, Prussian blue, etc.

(*c*) *Oil Substitutes* obtained by the action of sulphur monochloride on vegetable oils to reduce the specific gravity of low-grade goods.

(*d*) *Reclaimed Rubber* to cheapen goods where the addition of heavy mineral matter is not admissible.

The machine in which the mixing is carried out is similar in character to the "Washer," being provided with hollow rollers through which water or steam can be passed. Before the actual addition of the ingredients, the rubber is first "plasticized" by passing through the steam-heated rollers,

and when the rubber sheet is thin enough, the other materials are gradually added. It is the object of the mixer to obtain an homogeneous dough without overworking the rubber. For this purpose, the dough, while still hot, is passed through a "calender" machine, from which it is turned out in the form of a sheet, and led to a revolving wooden roll on which it is rolled between cloth. The "calender" consists essentially of superimposed smooth rollers, two or more in number, between which the rubber can be fed. The rollers are hollow for steam-heating.

If the rubber is not intended to be prepared in sheet form, the material from the mixing rollers may be passed into moulds or forced through a die, as when solid tyres and some forms of tubing are being made.

Vulcanization

This process is probably the most important that rubber has to undergo, and without it, it is doubtful whether any rubber industry, worthy of its name, could exist. The process consists in incorporating with the rubber, sulphur in its natural form, in solution or in combination such as polysulphides, and may be carried out by the hot or cold processes.

Hot Vulcanization or Hot Cure.—This process was discovered by Goodyear in 1839, and is carried out by intimately mixing rubber and sulphur by mastication. The process is facilitated by dissolving the rubber in naphtha and then mixing in sulphur. The temperature is raised to 100° C. At this temperature chemical union takes place between the constituents of the mixture, and vulcanized rubber is formed. The whole of the sulphur does not, however, combine with the rubber, but by prolonging the heating at 100° more and more of it enters into combination and a darker and tougher vulcanized product results. The action between the rubber and the sulphur does not start until the temperature reaches at least 100° C. Various temperatures ranging from 125°–300° C. are used, depending

on the form in which the sulphur is added, but for proper vulcanization it is essential that the temperature be above the melting point of sulphur, 114°. The best results are obtained when high pressure is used in conjunction with high temperature, and this is attained either by wrapping tightly with fabric—*e.g.* for hose and tyres—or by using an antoclave and injecting live steam.

Cold Vulcanization.—This process was discovered by Alexander Parkes in 1846, and is used more particularly for " proofing " cloth than for anything else. It is unsuitable for thick goods. It depends on the action of sulphur monochloride on rubber. This action is so violent, even in the cold, that the sulphur monochloride has to be diluted by dissolving in carbon disulphide before using. The process is carried out thus :—the rubber is plasticized, rolled out into a sheet and dissolved in naphtha with which it forms a sort of swollen dough. This is then rendered homogeneous by being worked between rolls and spread upon cloth by passing the latter between four series of rollers and a " doctor," which adjusts the thickness of the rubber. The solvent is removed by passing over a steam-heated table. The rubber-covered cloth is now conveyed to another machine upon which it is vulcanized by allowing it to unwind from one roller to another and making it pass over an intervening roller which dips into a sulphur monochloride bath.

The rate of vulcanization varies with the temperature and percentage of sulphur present. The natural proteids in the latex favour the cure as their removal retards the rate. Inorganic bases, like magnesia, were very early catalysts introduced to accelerate the hot cure, and in recent years organic bases have been used as accelerators. Piperidine was one of these which was first patented, but later the best results have been obtained by the use of aldehyde-ammonia.

Para-nitroso-dimethylaniline is another effective organic basic accelerator, the time for curing a mixture of 100 parts of rubber and 10 parts of sulphur at 140° C. being reduced from 1 hour to 20 minutes when 0·3–0·5 of this base is used in the mixture. If this substance be heated with

sulphur, unknown sulphur compounds are formed, which are also active accelerators. Twiss, arguing that the organic bases are active because of their solubility, claims that ordinary caustic potash dissolved in glycerine may be used instead of an organic accelerator as a vulcanizing catalyst.

Peachey uses sulphuretted hydrogen and sulphurous acid gas for cold vulcanizing.

Articles Manufactured

Cut Sheet.—This is used for tobacco pouches, surgical instruments, etc., and is made as follows: Rubber, after thorough washing, is masticated, and when homogeneous, is made into a solid mass and frozen hard. The mass is then sliced by a knife and the sheets vulcanized by the cold process.

Elastic Thread, for braces, garters, spring-side boots, etc., is made either by spreading or by calendering. In the "spreading" process several coatings of a dough consisting of rubber sulphur and naphtha are spread on to sized calico, and after dusting with French chalk, the rubber is stripped from the cloth, interlined with cloth and bound round a drum which is then vulcanized. After vulcanization, the rubber is removed from the drum, pasted over with a solution of shellac in methylated spirit, and, while still wet, wound round a roller so as to form a cylinder which dries to a compact block. The rubber is then placed in a cutting lathe and the thread cut out to the required gauge. To remove excess of sulphur and shellac, the threads are boiled in a solution of caustic soda. When made by "calendering," the procedure is exactly the same, only one starts with calendered sheet instead of spread sheet.

Tyres.—Solid Tyres, such as cab tyres, omnibus tyres, etc., are made by squirting an appropriate mixture through a die in a forcing machine. The dough is placed in a hopper, and by the motion of a screw, pushed through a die, from which it comes out as a long thick thread, which is coated with French chalk and wound on a tray. It is finally vulcanized by the hot process.

Pneumatic Tyres.—The *inner tubes* of pneumatic tyres

are usually made from calendered sheet by cutting to the desired length, lapping round a mandril and joining the ends together by means of a strip of rubber and rubber solution. Good results are also obtained by squirting as for solid tyres. The tubes are vulcanized with live steam on the mandril, and, after vulcanization, removed, and the ends joined up by means of rubber solution. Vulcanization is also sometimes done in moulds, collapse of the tube being prevented by having ammonia or ammonium carbonate between the walls. The method is carried out in the case of playing balls and other hollow articles.

Pneumatic tyre covers are made up on a mandril from proofed canvas and calendered sheet usually by hand and vulcanized in moulds in open steam.

Hose.—This is prepared from calendered sheet, proofed canvas and other materials in several ways, all more or less variations of one another. Thus "friction" hose is made by lapping alternate layers of calendered sheet and canvas round a long horizontal mandril, placed in a wrapping machine. The same result may be obtained by drawing a seamless (squirted) tube through a mandril and then lapping over with canvas, or by passing simultaneously a "squirted" tube and a canvas strip through a machine which folds the latter over the tube.

Buffers, Valves, etc.—Simple buffers are made by lapping over calendered sheet on a mandril until the requisite thickness is obtained and then vulcanizing in moulds. The finished article is sometimes made by cutting out of a vulcanized cylinder.

Belting.—This is made by spreading out a suitable dough on both sides of proofed canvas and cutting out into strips. The strips are joined together until a suitable thickness is obtained and vulcanized in a long hydraulic press.

Heels and Rubber Pads are made by stamping out of calendered sheet and vulcanizing in moulds.

Rings.—These are made either by joining together tape or cord, or by cutting from a tube on a lathe.

Ebonite and Vulcanite.—These terms are applied

to the product obtained when rubber is vulcanized for a prolonged time (six hours instead of two) with a very large excess of sulphur or sulphur-containing material (25–40 per cent. in place of the usual 5–10 per cent.).

The material is very hard, relatively non-elastic, but capable of being bent without breaking. It is capable of taking a high polish, may be turned on a lathe, softened by heat, moulded and pressed out, and is very indifferent to chemical reagents such as alkalis and acids. For this reason it finds extensive use in chemical factories for pumps, stop-cocks, and proof coverings, accumulator cases, etc.

It is prepared in a manner very similar to ordinary rubber goods, care being required to use the best materials possible, adding the foreign substances and then thoroughly mixing.

Gutta-percha.—This product is obtained from various East Indian trees by felling and ringing the bark at intervals of 12–18 ins. A latex oozes out which soon coagulates. This is then boiled, washed with hot water, strained, masticated between rollers and sheeted. Chemical cleansing with caustic alkalis or bleaching powder is sometimes used, and, when used for making a certain class of goods such as golf balls, etc., the resin which is present is extracted by treatment with petroleum spirit which leaves the gutta unaffected.

Gutta-percha proper is closely allied to caoutchouc, the active ingredient of ordinary rubber, but it is not identical with it. In physical properties it has very little resemblance to rubber. It has not the same elasticity, on warming becomes very plastic, and when pressed gives even the finest relief work in exact detail.

Under ordinary conditions, gutta-percha is hard but not brittle, forms an excellent insulator, and for this reason finds extensive use in submarine cables, being very resistant to high-water pressures.

Waste Rubber.—A very large quantity of scrap rubber is collected annually. The greater part is washed and ground up finely and used as a filler in low-grade goods, but the rest is reclaimed and used just like raw rubber. Various

processes are employed for effecting the reclamation, the most important being—

1. Washing to remove all dirt.

2. Treatment with alkalis and acids to remove fibre and metal particles.

3. Treatment with thiosulphate, sulphites, etc., to remove any uncombined sulphur and as far as possible devulcanize the rubber.

Rubber Substitutes

Owing to the high price which is paid for rubber, many attempts have been made to find substitutes which would not only resemble it but be cheaper to produce. The chief of these substitutes is that obtained from drying oils such as linseed, which is, of course, known to give an elastic film when it "dries."

When linseed oil is treated with sulphur (sulphur monochloride) or antimony sulphide, an elastic mass is produced which varies in colour according to the process used. These elastic masses are used as cheapening additions to raw rubber.

Other substitutes are obtained by heating together rape oil with sulphur, and castor oil with sulphur monochloride.

Mixtures of glue, gelatine, glycerine, oils, etc., after treatment with tannic acid, chromates, formaldehyde, have been used as substitutes for rubber.

In spite of all the work that has been done, no rubber substitute which can be used by itself, *i.e.* without any addition of rubber, is on the market.

Seeds and their Oils

A mature Hevea tree will produce on an average five hundred seeds per year, and as all these cannot under any circumstances be planted it is evident that a very large quantity of seeds must become available for commercial purposes every year.

The seeds must be collected, decorticated and dried before being transported, so that the question arises as to the commercial value of the oils from the seeds and the meal cake produced after the oil is pressed out from them. The collection is to a certain extent compulsory, as undergrowth and rodent life must be reduced to a minimum; decortication is necessary, as there is no other use for the shells, which weigh more than half the kernel, other than locally as fuel. Hence the value of the seed depends entirely on its oil and oil cake.

The fresh seed consists of about one-third shell and two-thirds kernel.

Composition of cake (kernel).

Moisture ..	9·1
Ash	3·53
Fibre	3·4
Oil	36·1
Proteins ..	18·2
Carbohydrates	29·67
	100·00

Hevea seed cake after expression of oil (kernel only).

Moisture ..	13·36
Ash	5·19
Fibre	5·00
Oil	6·00
Proteins ..	26·81
Carbohydrates ..	43·64
	100·00

It is evident, therefore, that the kernels contain about one-third their weight of oil.

The oil is clear, light yellow in colour, and on saponification with soda yields a soft soap. It has been stated that it can be used for the preparation of varnishes, and further investigations have shown that it is suitable as a substitute for linseed and similar drying oils. Little seems to have been done on the lines of utilizing this oil, owing probably to high cost of seed collection and the fact that it would have to compete with other oils on the market; but, given local seed pressing machinery, there seems to be no reason why this source of wealth should remain undeveloped. See further, p. 56.

Ceara Rubber Seeds.—These are small hard seeds weighing about 53 gms. per 100. They are difficult to shell, mincing processes giving only 45 per cent. kernel. The shell so obtained is unsuitable for cattle feeding unless finely ground.

The oil amounts to 35 per cent. of the kernel, but only 15 per cent. on the whole seed. It has a light yellow colour, agreeable odour and taste and resembles linseed oil in having a high iodine value, drying quickly and giving a tough elastic skin very white in colour. On boiling it becomes very viscous and forms a transparent gelatinous mass when treated with sulphur chloride.

Funtumia elastica.—These are small pointed seeds with husks thin and soft. One hundred seeds weigh about 5 grams. The oil is very dark in colour and amounts to 33 per cent. on the seed. Ordinary decolorizing agents have little effect on it. It froths on boiling and has a bitter odour and taste, and deposits mucilaginous matter accompanied by stearine in cold weather. It has the properties of a drying oil, but gives a tacky film. On heating it darkens in colour, and forms a viscous liquid similar to linseed oil freshly extracted. Treatment with sulphur chloride gave an elastic but sticky substance.

The physical and chemical properties of these oils compared with linseed and Hevea oils are given below:—

	Ceara.	Funtumia.	Hevea.	Linseed.
Weight of 100 seeds ..	53·2	4·8	360 gms.	—
Oil content of kernel ..	35·0%	—	45·48%	—
„ „ of total seed	15·75%	31·0–33·0%	22·25%	36·40%
Sp. gr.	0·9238	0·9320	0·9258	0·931–·938
Refractive index (15° C.)	1·475	1·4788	—	1·4835
Relative viscosity ..	13·0	14·3	—	18·0
Iodine value	135·0–137·0	138·0	138·7	180°–200°
Saponification value ..	189·1	185·0	191·2	190–195
Acid value	0·625	2·65	5·26	below 5
Hehner value	95·1	94·0	—	94·81–95·5
Reichert-Meissl ..	0·44	0·66	2·7	0·00
Liquid fatty acids ..	88·9%	79·8%	86·0%	92·5%
Iodine value thereof ..	162·5	175·5	—	190°–210°

FAT-FREE RESIDUE

	Per cent.	Per cent.
Nitrogen	2·19	4·34
Proteins	14·23	27·08
Ash	17·10	5·04
Potash	2·65	1·44
Phosphoric acid	1·72	2·25
Sand	0·72	0·32

Diseases and Pests

The fungoid diseases of Hevea have been carefully studied both in Ceylon and in Malaya, and many of them seem to be identical. From time to time certain of these diseases become more virulent and attract greater attention, but on most estates the treatment is known, and a sharp look-out is kept which makes the mortality from fungoid diseases not a serious factor. The root diseases are those which are chiefly to be feared, as in many of them the mycelium travels through the soil and thus spreads the disease from tree to tree. Isolation by digging a trench round the tree and the excision of all the infected roots with subsequent burning is the treatment in the early stages. The roots of neighbouring trees should, however, be examined to be sure that the fungus has not reached them. The common root diseases are due to *Fomes lignosus* (formerly, semitostus), *Ustulina zonata* (which originally was studied in its ravages on tea), *Poria hypolateria* (known as hypobrunnea in Ceylon), *Sphaerostilbe repens* and *Hymenochaete nexia* or brown root disease. Diseases affecting the bark and leaf surface are more easily detected. In districts with a heavy rainfall, *Pink disease,* caused by *Corticium Salmonicolon,* appears on the underside of the bark of the stem and branches of the Hevea. This fungus also grows on most tropical plants and has caused trouble on coffee, tea, cinchona and other plantations.

Synthetic Rubber

Synthetic rubbers have been prepared in the laboratory by the polymerization of unsaturated hydrocarbons. This change is hastened by catalysts. As far back as 1860, Greville Williams noticed that isoprene which he obtained by distilling rubber, reverted back into a viscous solid on keeping, and in 1879 Bouchardat found that in presence of hydrochloric acid, the same condensation took place more

rapidly. Piperylene, an isomer of isoprene, behaves similarly. Tilden found that nitrosyl chloride also acted as a catalyst in polymerizing isoprene to rubber, and in 1892 showed that this synthetic rubber could be vulcanized. About the same time, Couturier proved that dipropylene similarly polymerized by heat to a solid rubber, and Matthews, in 1910, patented the use of sodium for bringing about the polymerization of butadiene (erythrene) and its homologues. In this way, 20 parts of isoprene, mixed with 1 part of sodium, in the cold becomes solid, and any unchanged liquid can be distilled off or extracted by a suitable solvent. Harries confirmed this useful catalytic property of sodium on these unsaturated hydrocarbons, and more recently, acetic anhydride at 150° has been patented for the conversion of isoprene to rubber, and even small quantities of acid or sulphur promote the condensation when heated with the hydrocarbon. Oxygen carriers, sodium or zinc ethyl and colloidal metals are also the subject of other processes for bringing about this change.

Ostromyslenski, in Russia, during the war suggested that isoprene could be catalytically converted first into β-myrcene, and that this new hydrocarbon could be finally condensed to caoutchouc, having all the properties of Para rubber.

Much further study is required as to the yields obtained by these various processes before one can predict which is likely to be economically successful.

The source of the parent isoprene or other unsaturated hydrocarbon and cost price of the same has also to be considered before one can arrive at any measure of the future possible competition between synthetic caoutchouc and that obtained from plantations. These parent hydrocarbons are now obtainable by the removal of water by passing ketones or alcohols over suitable dehydrating catalysts. Thus, starting with dihydroxymethyl butane one can obtain the corresponding ketone and finally isoprene by using, according to one patent, aluminium silicate as the catalyst at

a temperature between 400° and 600° under diminished pressure.

$$CH_2OH.CH(CH_3).CHOH.CH_3 - 2OH_2 = CH_2{:}C(CH_3).CH{:}CH_2$$

If an ester like the acetate of methyl butenol be heated with alumina under diminished pressure to 400°, acetic acid and isoprene are formed.

$$CH_3.C(CH_3).(OCOCH_3).CH : CH_2 = CH_3.COOH + CH_2 : C(CH_3).CH : CH_2$$

Ostromyslenski starts from acetaldehyde and an alcohol with a catalytic dehydrating agent, such as precipitated alumina which owes its activity to traces of basic salts, thus—

$$CH_3.CHO + CH_3.CH_2OH = 2H_2O + \underset{\text{Erythrene.}}{CH_2 : CH.CH : CH_2}$$

$$CH_3.CHO + (CH_3)_2CHOH = 2H_2O + \underset{\text{Piperylene.}}{CH(CH_3){:}CH.CH{:}CH_2}$$

The best yields seem to be not more than 16–18 per cent. of the pure hydrocarbon.

These syntheses of the butadienes thus put the parent material a stage further back to the alcohol or ketone, and it is still doubtful whether these can be obtained commercially say, from starch, by fermentation or by a synthesis from carbide at such yields and at a price which would enable an industrial development to follow.

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PATENTS BEARING ON THE MANUFACTURE OF SYNTHETIC RUBBER.

English Patents. 1907: 21772; 1908: 13252; 1909: 15299, 29277, 29566; 1910: 4001, 4189, 4572, 4620, 5931, 5932, 8100, 9219, 14040, 14041, 15254, 17734, 24790, 25850; 1911: 1124, 1125, 6540, 9721, 9722, 15203, 15204, 16925, 18935, 27361.

French Patents. 1911: 434586, 433825, 433322; 1912: 438789, 277, 448, 3873, 5555, 12770, 12771, 12772, 12773, 13051; 1914: 47565.

German Patents. 1913: 286640; 1914: 279780.

Part II.—DRYING OILS

The class of oils which the paint and varnish maker uses show the property of "drying" in the air. The drying of a film of paint or varnish depends primarily on the nature of the vehicle. The difference can be shown by an experiment whereby plates of glass are coated respectively with water, petrol, kerosene or paraffin and linseed oil. After several days' exposure the petrol and water will have evaporated, while the plate coated with kerosene will be found to be greasy and almost unchanged. The linseed oil coating will have become tacky and will finally set to a tough varnish-like film. Linseed oil is a typical drying oil. Some oils, *e.g.* olive oil and castor oil, will behave like the paraffin layer and are non-drying oils. Semi-drying oils will become tacky very slowly and may, on prolonged exposure, yield flexible films. This property of drying can be accelerated by incorporation of "driers," to which fuller reference will be made later. In spite of the vast quantities of linseed and other drying oils handled annually the changes occurring during the "drying" are not fully understood. Undoubtedly linseed oil is the most important member of its class, and its general properties may be considered typical. It contains the glycerides of unsaturated acids of the aliphatic series, with 18 carbon atoms in an open chain. It is of interest to record that no drying oil of vegetable origin is known derived from an acid containing less than 18 carbon atoms in the molecule (isanic acid $C_{14}H_{20}O_2$ is perhaps an exception). The majority are open-chain compounds with the exception of the oils from chaulmoogra seeds (Barrowcliff and Power, *J. Chem. Soc.*, 1907, *101*, 577). As glycerides they are saponifiable and are "fatty" oils in

contradistinction to mineral oils, which are unsaponifiable. They may also be termed fixed oils, in that they cannot be volatilized under atmospheric pressure without decomposition. The drying oils of animal origin (menhaden and Japanese fish oil) contain the glyceride of clupanodonic acid, $C_{18}H_{28}O_2$, whilst the liver oils of certain members of the shark family contains spinacene, a highly unsaturated hydrocarbon (Chapman, *J. Chem. Soc.*, 1917, *111*, 56). It is possible that this substance is identical with squalene, also present in shark oil (Tsujimoto, *J. Ind. Eng. Chem.*, 1916, *8*, 889).

One characteristic difference between animal and vegetable oils, including drying oils of animal and vegetable origin, lies primarily in the presence of cholesterol, $C_{27}H_{45}OH$ (an alcohol), which is a component of the well-known lanolin; whereas vegetable oils contain phytosterol (an alcohol of the same formula), which is distinguishable under the microscope and yields an acetate with a melting point different to that obtained from cholesterol.

Genuine linseed oil is essentially a mixture of the triglycerides of linolenic, linolic, and oleic acids, together with small quantities of glycerides of saturated aliphatic acids, palmitic, stearic, and possibly myristic acids. The glycerides are mixed glycerides of varying composition depending on the source of origin and on the maturity of the seed from which the oil has been expressed. The amount of saturated glycerides is small, but their presence in linseed oil is a factor for consideration in any varnish process.

Friend, "Chemistry of Linseed Oil," 1917, p. 64, summarizing the evidence up to date, states the percentage composition as follows:—

Saturated organic acids	10·0	10·0
Oleic acid	5·0	5·0
Linolic acid	48·3	59·1
Linolenic acids	32·1	21·3
Glyceryl radicle (C_3H_5) ..	4·6	4·6
Total ..	100·0	100·0

Fahrion (*Z. angew. Chemie.*, 1910, *23*, 722 and 1106) gives a slightly different composition :—

Unsaponifiable matter	0·6	per cent.
Saturated fatty acids	8·6	,,
Oleic acid	15–20	,,
Linolic acid	30	,,
Linolenic acids	38	,,

The most important component of linseed oil is the glyceride of linolenic acid, $C_{17}H_{29}COOH$, or

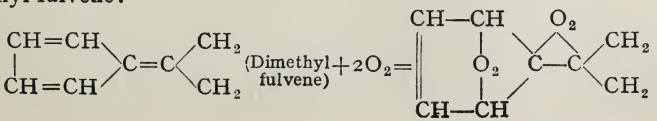
$CH_3CH_2.CH=CH.CH_2.CH=CH.CH_2.CH=CH(CH_2)_7COOH$

(Goldsobel, *J. Russ. Phys. Chem. Soc.*, 1906, *38*, 1904; 1910, *42*, 55; Erdmann and Raspe, *Ber.*; 1909, *42*, 1334; Erdmann and Bedford, *Ber.*; 1909, *42*, 1324.)

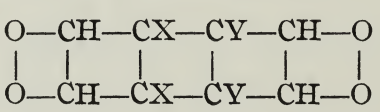
Stearic acid is a saturated acid possessing the formula $CH_3(CH_2)_{16}COOH$.

Linolenic acid is stated to occur in two forms in linseed oil, as glycerides of α and β-linolenic acid (Erdmann and Bedford, *loc. cit.*). From the work of Erdmann and his collaborators linolenic acid may be taken as containing three double linkages as shown above. From the general properties of such a configuration it is to be expected that the oxidation of linolenic acid will proceed in stages, whereby a molecule of oxygen becomes attached where there is a double linkage. This gradual absorption has been observed in the oxidation of China wood oil (*J. Chem. Soc.*, 1918, *113*, 111). Peroxides of the type $\begin{matrix}O—CH\\|\\O—CH\end{matrix}$ are formed (Fahrion, *Chem. Zeit.*, 1904, *28*, 1196; Wilson and Heaven, *J. S. C. I.*, 1912, *31*, 565; and Ingle, *J. S. C. I.*, 1913, *32*, 639), and eventually from the linolenic acids there result glycerides of diperoxylinolenic acids when linseed oil is transformed into the highly oxidized state of linoleum (A. de Waele, *J. Ind. Eng. Chem.*, 1917, *9*, 1).*

* Cf. Engler and Frankenstein, *Ber.*, 1901, *34*, 2933, on the oxidation of dimethyl fulvene:—



The relative positions of the peroxide attachments is not definitely fixed, but it may be presumed that they are contiguous to the $(CH_2)_7COOH$ group end of the chain. Ingle (*J. S. C. I.*, 1902, *21*, 594) states that the doubly linked carbon atoms in proximity to COOH groups may be prevented from absorbing halogens from a strongly acid Hübl solution. Such peroxides may undergo subsequent polymerization (Fahrion, *Chem. Zeit.*, 1904, *28*, 1196, and Morrell, *loc. cit.*) which may occur by linkage up of the molecules through unattacked, unsaturated carbon atoms, rather than through the peroxide groups :—



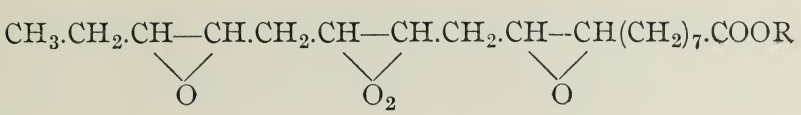
Linking up through unsaturated carbon atoms is more likely because of the probable occurrence of the glyceride of diperoxylinolenic acid in linoleum (*loc. cit.*) rather than a triperoxy-acid, and also the subsequent polymerization of monoperoxy-α-elaeostearic acid obtained from tung oil. It must be pointed out that these peroxides are unstable and their possible products will be discussed later.

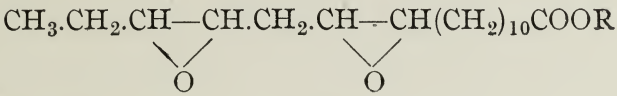
Fokin (*J. Russ. Phys. Chem. Soc.*, 1908, *40*, 276) considers that the primary product in the oxidation is an oxide R.CH—CHR

. General evidence favours a peroxide formula for the oxidation product of linseed oil, but the subsequent change to linoxyn may be accompanied by polymerization or by decomposition of the oxidized molecules with polymerization of the products (Harries, *Annalen*, 1906, *343*, 318) ; and A. de Waele, *Chem. World*, 1914, *3*, 300).

Salway (*J. Chem. Soc.*, 1916, *109*, 138) suggests that linoxyn consists of olein and of polymerized aldehydes derived from the decomposition of the oxidized linolenin. De Waele considers it to consist of peroxides with polymerized aldehydoglycerides (*loc. cit.*). Orloff (*J. Russ. Phys.*

Chem. Soc., 1910, *42*, 658) suggests that linolenic and linolic glycerides on oxidation yield respectively :—



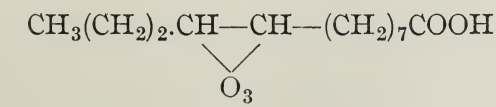


These formulæ do not account for the presence of unsaturated components of linoxyn. [See also "Theory of Driers."]

Without going further into the undecided changes in the oxidized molecule, it is sufficient to state that the tough elastic film obtained when linseed oil is oxidized is linoxyn, and that it contains the glyceride of diperoxylinolenic acid with possibly some peroxylinolic acid glyceride, together with their decomposition products.

The systematic examination of the oxidation products of linseed oil is comparatively recent, in spite of the great antiquity of its employment in the arts and crafts.

The conditions of absorption of oxygen will be discussed under the theory of driers, but it will be of advantage to study briefly the reactions of unsaturated glycerides, so as to understand the behaviour of drying oils. The researches of Harries and his pupils (*Ber.*, 1906, *39*, 2894, and 1909, *42*, 442), Molinari (*Ber.*, 1906, *39*, 2735, and 1908, *41*, 2794), Erdmann and Raspe (*loc. cit.*), and Fenaroli (*Gazz. chim. ital.*, 1906, *36*, (2), 292) on the action of ozone on unsaturated acids and oils have shown that a molecule of ozone can be attached to each pair of doubly linked carbon atoms. Such ozonides, *e.g.* oleic acid-ozonide



are easily decomposed by water and by alkalies to give acids and aldehydes according to the scheme—

$$R.CH(O_3)—CH.R'.COOH \rightarrow \underset{\text{Acid.}}{R.COOH} + \underset{\text{Aldehydo acid.}}{CHO.R'.COOH}$$

$$\rightarrow RCOOH + \dot{R}'(COOH)_2 \quad \text{(Dibasic acid)}$$

The identification of the products of decomposition has thrown light on the structure of the unsaturated acids, and Erdmann and Raspe's formula for linolenic acid rests on the results of such an investigation. For details as to the properties of the ozonides and their importance in fixing the structure of linseed and other oils, reference may be made to Friend's monograph on the "Chemistry of Linseed Oil," 1917, pp. 18, 44, which is supplied with an excellent bibliography on the subject.

In addition to ozone, hydrogen may be made to unite with glycerides of the unsaturated oil acids by modifications of Sabatier and Senderens' method, whereby hydrogen is absorbed in the presence of nickel as catalyst, with the formation of a saturated acid or its glyceride, viz. stearic acid

$$X—CH=CH.Y + 2H = X.CH_2—CH_2.Y$$

The hardening of oils, whereby the liquid fat is transformed into solid stearin, is now an important industry which may be said to date from the time when the scientific investigation of oils was systematically undertaken. The reduction is quantitative, and Bedford (*loc. cit.*) has demonstrated that the hydrogen absorbed can be taken as a measure of the degree of unsaturation of the oil; this is usually decided by the determination of the iodine value, which has now become a recognized method for the examination of drying oils.

$$X—CH=CH—Y + 2I = X—CHI—CHI.Y$$

The iodine is usually presented in the form of ICl and the excess determined volumetrically (Fryer and Weston, "Oils, Fats, and Waxes," 1918, *2*, 94). Sufficient has been given to indicate the unsaturated character of linseed oil as a typical

drying oil as shown by its power to absorb elements such as oxygen, hydrogen, chlorine, bromine and iodine.

If a layer of linseed oil (0·1–0·2 gram per 100 sq. cms.) be spread on glass, the maximum gain in weight is 19 per cent. of the weight of the oil taken (Lippert, *Z. angew. Chem.*, 1898, *11*, 412; Weber, *ibid.*, 508). The rate of absorption depends on the temperature, atmospheric conditions and on the presence of catalysts or "driers." The absorption is accompanied by a decomposition due to the degradation of the peroxides previously referred to. The decomposition products comprise volatile substances, *e.g.* carbon dioxide, water, formic and acetic acids, aldehydes (acrolein, C_3H_4O) (Salway, *Trans. Chem. Soc.*, 1916, *109*, 136), caused by the disruption of the molecule where the oxygen has been attached to the double linkages. Such aldehydes may have a bactericidal action, and if present in large concentration they are considered by some to have toxic properties.*

Moisture and soluble ferments bring about hydrolysis of the glycerides whereby acids are formed, which on oxidation and rupture of the molecule produce aldehydes causing "rancidity" (Nicolet and Liddle, *J. Ind. Eng. Chem.*, 1916, *8*, 416).

Owing to the loss of volatile products the percentage of oxygen absorbed after 56 days' exposure may be 2·25 times the observed increase in weight of the oil, if it is allowed free exposure to air and no film is allowed to form.

(1) Time of exposure, 56 days; increase in weight of the oil, 9·74 per cent.; weight of volatile products, 12·2 per cent.; weight of oxygen absorbed, 21·49 per cent.

(2) Time of exposure, 68 days; increase in weight of the

* It is significant that no evidence has been shown of the toxicity of the gases evolved during the oxidation of linseed oil in enclosed spaces, such as are found in the "oxidizing sheds" in linoleum works (see chapter on Linoleum). The concentration of the vapour evolved in these chambers where solidification of linseed oil at the rate of one ton per diem takes place, is such that their irritant effect on the mucous membrance of the nose, and the lachrymatory glands of the eyes, make it impossible for any but operatives inured to the vapours to withstand them with comfort for more than a minute or so. Workmen employed in the oxidizing sheds are said to remain in them for periods of an hour at a time, without suffering any ill effects other than a passing discomfort due to hypersecretion of the glands mentioned.

oil, 8·96 per cent.; weight of volatile products, 15·8 per cent.; weight of oxygen absorbed, 24·77 per cent. (Friend, *Proc. Paint and Varnish Soc.*, May 14, 1914; Wilson and Heaven, *J. S. C. I.*, 1912, *31*, 565; and de Waele, *Chem. World*, 1914.)

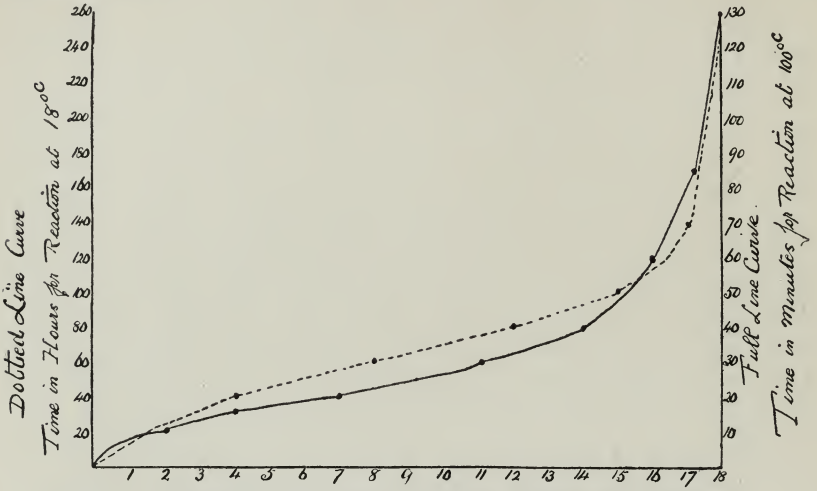


FIG. 1.—Percentage of Oxygen absorbed (Wilson and Heaven).

From the above data there is a point of equilibrium at which the gain in weight is approximately equal to the loss

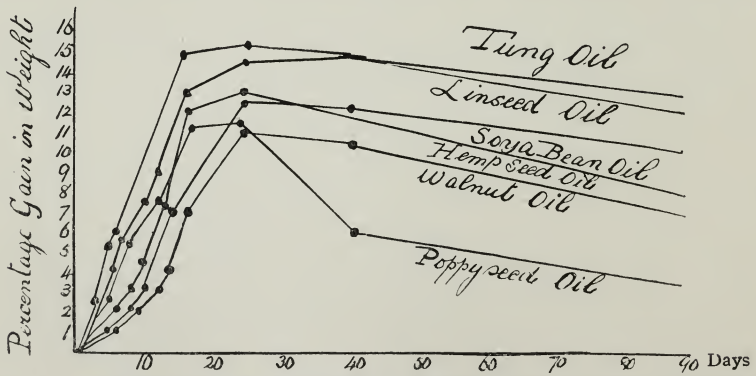


FIG. 2.—Percentage Gain in Weight of Drying Oils at Room Temperature (Friend).

in weight due to escaping vapours and gases. Any factor assisting or retarding the removal of the oxidation products will proportionally lower or raise the observed increase in

the weight of the oil; this accounts for the varying figures given, 13–25·6 per cent. (Ingle, *J. S. C. I.*, 1913, *32*, 639, and Redman, Weith, and Brock, *J. Ind. Eng. Chem.*, 1913, *5*, 630.)

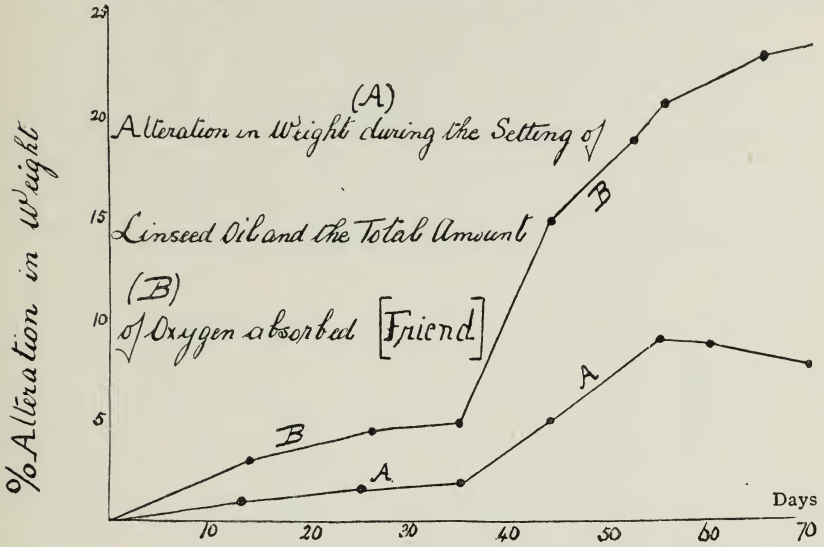


FIG. 3.

The increase in weight of some drying and semi-drying oils on exposure to air is shown in Figs. 1, 2, and 3.

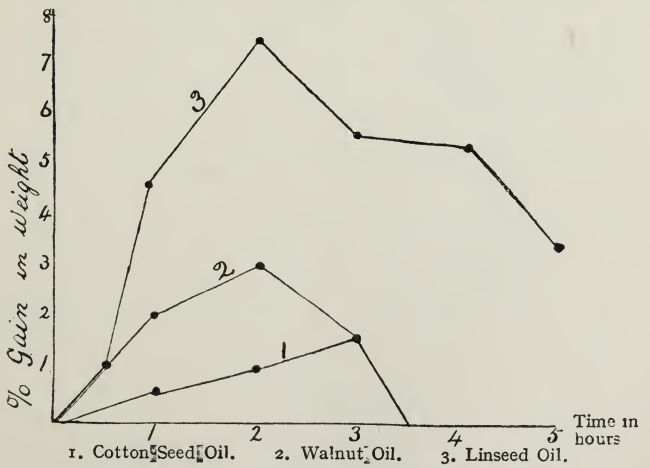


FIG. 4.—Rate of Percentage Gain in Weight of Oils at 100° C.

In Figs. 1 and 2 the variation of the percentage of oxygen absorbed and the increase in weight of linseed

oil with the time of exposure are shown. In Figs. 2 and 5 a comparison is given between drying oils and semi-drying oils, as to the weight of oxygen absorbed with the time.

In Figs. 4 and 5 the effect of temperature on the rate of absorption by three oils, of which cotton seed oil is a typical semi-drying oil. From an examination of the curves there is evidence of an induction period during which the increase in weight is slow. It is assumed that small quantities of peroxides are being produced which, on their formation, act catalytically as oxygen carriers. The addition of a metallic

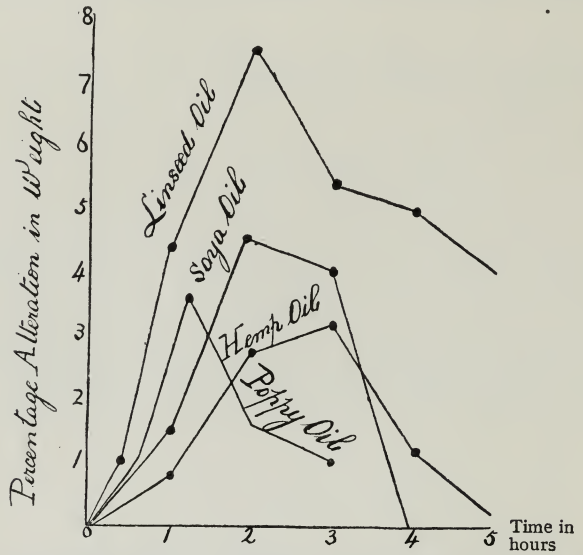
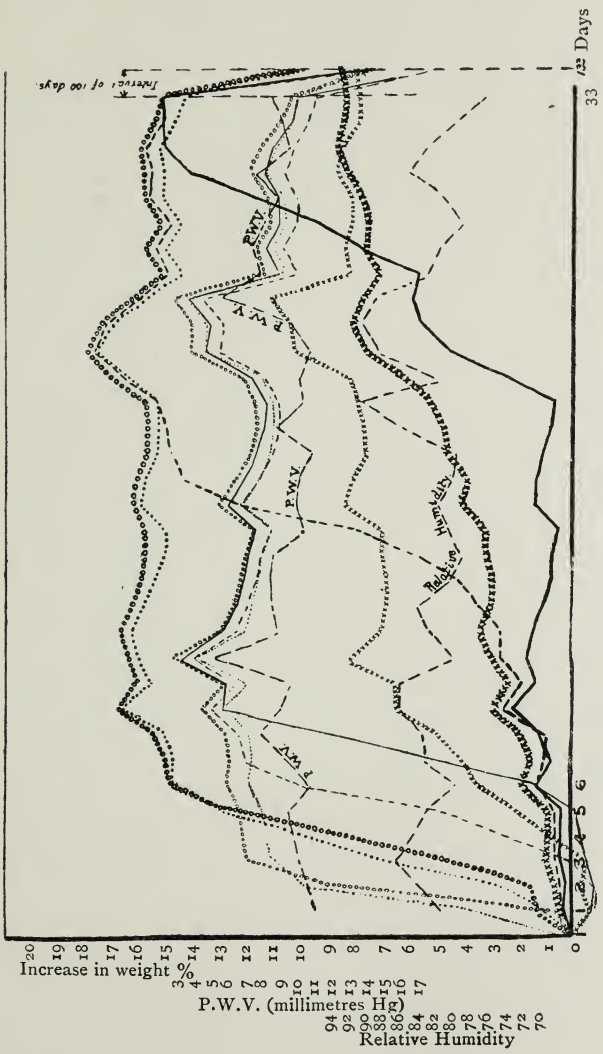


FIG. 5.—Percentage Gain in Weight of Drying Oils at 100° C. (Friend).

drier reduces this induction period. Fokin (*J. Russ. Phys. Chem. Soc.*, 1907, *39*, 607, and 1908, *40*, 276) states that the rate of setting of linseed oil films follows Spring's rule, in that it is doubled for every 10 degrees rise in temperature; moisture retards the time of setting. It is evident that the change cannot be expressed by a simple velocity equation because of the loss of volatile products and the possibilities of polymerization of the oxidizing and oxidized oil. Polymerization would tend to reduce the amount of the volatile products.

The influence of moisture is shown in Fig. 6.

The curves in Fig. 6. (A. de Waele, *J. S. C. I.*, 1920, *39*, 48T) represent graphically the results obtained by plotting the variations in weight shown by exposing variously


Days
Raw Linseed Oil (no drier).
" " " containing 0·1% Mn.
" " " 0·5% Pb.
" " " 0·1% Pb and 0·0023% Mn.
Polymerized Linseed Oil free from oxidized oil or drier.
Increase in weight %
P.W.V. (millimetres Hg)
Relative Humidity

The light and heavy lines represent exposures in daylight and darkness respectively.

FIG. 6.

treated linseed oils in air, the atmospheric conditions being simultaneously plotted as detailed in the graph. It will be noticed that the two series of observations, viz. in light and in darkness, although agreeing in the direction of the

path of the curve followed by the individual oils examined, differ very materially, a fairly close connection existing between the inverse of the pressure of the water vapour and the light conditions, whilst the darkness conditions follow more closely the relative humidity readings. The coincidence of the paths followed by the different oils occurs after the completion of the first induction period. The relative stability of polymerized oil is shown by the steady upward tendency and closeness of the ordinates at the 33rd and 133rd day periods, and further supports the view as to its constitution outlined on p. 37. The conclusions drawn by the author from the above curves are that the periodic variations in weight are caused by the two factors composing the atmospheric conditions: (1) The decomposition of the primarily formed peroxides is initiated by the presence of water; and (2) equilibrium conditions, *i.e.* decomposition *versus* back-pressure, are attained by the interpretation of the latter as pressure of water vapour.

Gardner (*Circular No.* 70, *Paint Manufacturers Assoc. of the U.S.*), discussing variation in weight curves showing two alternate increases and decreases, holds the view that the first decrease is represented by decomposition of the oxidized product into volatile products and solid oxidized residue, followed by splitting up of the latter into fatty acid and the glyceryl radicle, the glyceryl then taking up water to form glycerol and thus representing the second increase. The second decrease is then held to be accounted for by decomposition of the glycerol into volatile decomposition products.

The effect of stoving a linseed oil film at 100° C. is to increase the water-resisting power by increasing the thickness of the layer of linoxyn. Friend has found that a film of linseed oil dried at 15° C. absorbed five times as much moisture as a similar film stoved at 100° C. (*J. Iron and Steel Institute*, 1911, iii. 54). He states that the painting of wrought iron while it is hot gives a much more effective protection.

Genthe (*Z. angew. Chemie*, 1906, *19*, 2087), Fig. 7, showed that the rate of oxidation of linseed oil exposed to ultra-violet

light was greatly accelerated. In the dark the maximum absorption was reached in 50 days, whereas when exposed to light from a mercury lamp the maximum was attained in 25 hours. Under these conditions linseed oil was found to absorb 34 per cent. of its weight from the atmosphere.

Changes in weight are accompanied by changes in volume. Friend (*Trans. Chem. Soc.*, 1917, *111*, 162) found that with increase in weight (17·9–18·5 per cent., *i.e.* solid linoxyn), there was an increase in density with an increase in volume up to 3 per cent.; subsequently a contraction ensues on long exposure which is a simple explanation of the

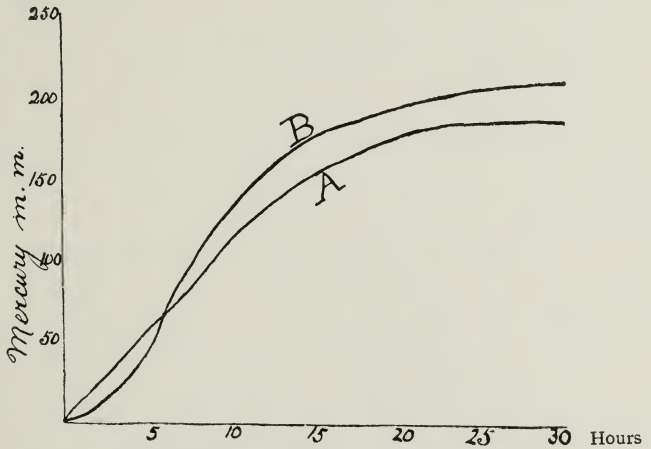


FIG. 7.—"A" = Linseed Oil } Exposed to light
"B" = Blown Linseed Oil } mercury lamp (Genthe).

cracking of paints and the shrivelling of varnishes. Wolff (*Farb. Zeit.*, 1919, *24*, 1119) has found that where varnishes yield glossy films in light of short wave-lengths, shrivelled films are produced in light of long wave-length. He maintains (*loc. cit.*, 1389) that in varnishes exposed to light of short wave-length oxidation and polymerization proceed at nearly equal rates, whereas in light of long wave-length polymerization is retarded more than oxidation, so that inequality in volume of inner and outer layers is produced.

Gardner (*J. Ind. Eng. Chem.*, 1914, *6*, 91) has shown that linseed oil, when mixed with chemically inert powders such as barytes and silica, exhibited a smaller gain in weight on

setting, the powders apparently assisting in the decomposition of the peroxides with the production of volatile material.

The absorption of oxygen is accompanied by an evolution of heat, so that precautions must be taken to avoid spontaneous combustion of any fabric impregnated with a drying oil (Mackey and Ingle, *J. S. C. I.*, 1917, *36*, 319). Similarly the absorption of bromine by linseed oil is exothermic, and Marden (*J. Ind. Eng. Chem.*, 1916, *8*, 121) states that 206 calories per gram of linseed oil are evolved, compared with 100·7 calories in the case of olive oil.

After the general statement of the properties of linseed oil as a drying oil, it will be advisable to describe briefly the sources of the seed, and the mode of extraction of the oil.

On the importation of linseed depends the supply of paint in the building and decorating trades, and for the manufacture of linoleum, although abroad linseed oil is used to a very limited degree as a burning oil; during the war it was an important source of glycerine.

IMPORTS FOR CONSUMPTION OF OIL SEEDS IN 1913.

	Linseed.	Soya beans.
United Kingdom ..	654,812 tons	76,452 tons
United States ..	132,357 ,,	Not separately distinguished
Germany	560,323 metric tons	125,750 metric tons (including castor oil)
France	237,406 ,, ,,	45
Belgium	259,105 ,, ,,	Not separately distinguished

1913 was considered to be an abnormally high year for linseed.

On conversion of the seed into oil values and deducting the figures for re-export, so far as the United Kingdom is concerned, Mr. Pearson, chairman of the Oilseed Crushers Association, has compiled the following table for 1912–14, 1915, and 1916.

	Oil imports or equivalent of seed imports.			Oil exports.			Oil retained for U.K.		
	1912–14.	1915.	1916.	1912–14.	1915.	1916.	1912–14.	1915.	1916.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Linseed oil	158,124	123,554	151,710	275,562	55,927	24,761	130,562	67,627	126,949
Cotton seed oil	127,510	117,911	60,212	26,360	36,082	3,397	101,150	81,829	56,815
Fish oil	63,811	91,872	109,061	8,229	4,570	1,146	55,582	87,302	107,915

During the war the demand for oil seeds was increased by three main causes: (1) the demand for glycerine for explosives, which involved splitting a quantity of oil far exceeding the normal requirements of the soap trade. (2) The demand for edible oils for margarine. (3) Maintenance of the supplies of feeding cake for cattle.

Fortunately the British Empire possessed the very substantial advantage that the supply of oil seeds generally was amply sufficient for the requirements, and left a margin for export, as shown in the table given above. By the system of prohibiting exportation from countries of origin to destinations other than the United Kingdom or the Allies, except under special licence, it was possible to secure to this country any quantities required for which shipping was available.

The largest exporting countries of linseed are the Argentine, Russia, India, and Canada. The general oil-seed production of India is already very great, and is capable of still further increasing ("Oils and Fats in the British Empire," Sir A. D. Steel Maitland, 1917). The Canadian crop is absorbed by the United States. The Argentine exports to Europe reached in 1913, 1,100,000 tons, or on the average 800,000 tons annually. The exportable surplus from India varied from 250,000 tons to 400,000 tons in 1913.

Small quantities have been grown in England with very satisfactory results (Eyre and Morrell, *British Flax and Hemp Growers' Society Publications*, 1919, and *J. Board of Agriculture*, 1919). China is becoming a linseed oil seed exporting country. Soya bean from China, Manchuria, and Japan have become less popular, and have fallen from 400,000 tons in 1910 to a much lower figure.

The flax or linseed plant (*linum usitatissimum*) is grown in some countries for fibre, and the highest germinating seeds are preserved for sowing. The true flax-bearing plant has a straight, unbranched stem, 40 inches high, consisting of a core, an outer covering, and an intermediate layer of bast tissue. It is the bast tissue which gives the flax fibre,

after separation by retting and scutching, to be spun for linen. The seed variety is branching and shorter in the stem, and its fibre is of relatively small importance. The yield of seed per acre from the flax plant is 6–10 cwt., while the seed variety gives 10–20 cwt. per acre. The seed from the branching variety is larger and yields 30–40 per cent. of oil. To extract the oil from the seed hot or cold pressing may be employed, the former being the most common, while the latter is only resorted to when a pale edible oil is required, as in Russia, Germany, and India.

Extraction of Linseed Oil.—The extraction of oils from their seeds is essentially an engineering problem. The broad, general methods are two, viz. employment of pressure and extraction by solvents. As the seeds are small they are crushed in hydraulic presses and the oil forced out of the seed. The seed or meal is heated during the process of hot crushing, and the oil produced is known as hot-pressed or hot-drawn oil. Such oil is discoloured by its having dissolved, during the expression, an excessive amount of colouring matter. The cold-drawing process leaves usually a considerable amount of oil in the cake, but it is freer from impurities such as mucilage, and is of a better colour. By either hot or cold process not more than 90–95 per cent. of the total oil is removed from the press-cake. The second process extracts all the oil from the seed by the use of solvents, benzol, carbon disulphide, or carbon tetrachloride. The process in outline consists in allowing the solvent to percolate through the seed or meal in a closed vessel, drawing off the solution and distilling off the solvent.

Anglo-American Crushing System.—Linseed, rape seed, and similar small seeds do not entail preparatory machines to reduce them to a form suitable for treatment in the subsequent oil recovery process. Such machines are specialized and are designed to deal with one particular class of seed or nut, *e.g.* for reducing copra and converting it to meal (Fig. 8).

The oil seeds (linseed, rape, etc.) are first passed through a magnetic separator to remove pieces of metal which

have been added to bring up the weight of the seed, and then pass by an endless band conveyor to the crushing mills.

Seed Crushing.—This operation is performed by a crushing mill which consists of 5 rolls, 16 inches in diameter and 42 inches long, stacked vertically, and are quite plain on the sur-

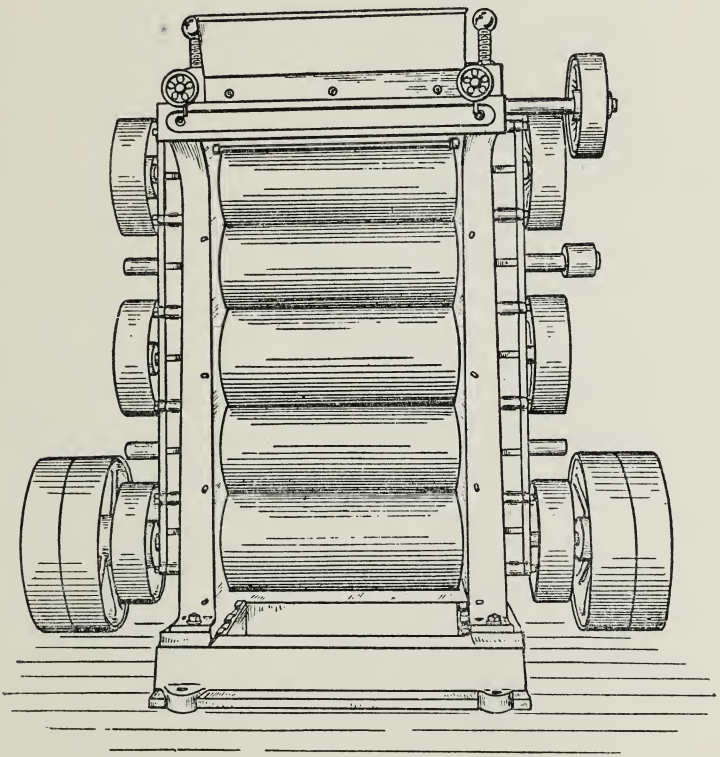


Fig. 8.—Anglo-American Rolls. (Rose, Down and Thompson, Ltd., Hull.)

face. As usual they are ground very true and are forced on to their shafts by hydraulic pressure, and thereafter keyed at both ends. The lowest roll is driven at both ends and is provided with two additional pulleys, from which belts are taken to similar sized pulleys at each end of the third and fifth rolls. The bearings for all the rolls except the lowest are free to slide vertically in their housings, so that the pressure exerted on the seed increases with each step in its

descent. The capacity of the rolls is about 15 cwt. per hour.

Heating and Moulding.—The heating of the crushed seed or meal facilitates the expression of the oil, helping to rupture the cells in which the oil is contained; moreover, the viscosity of the oil is reduced so that on pressing it flows

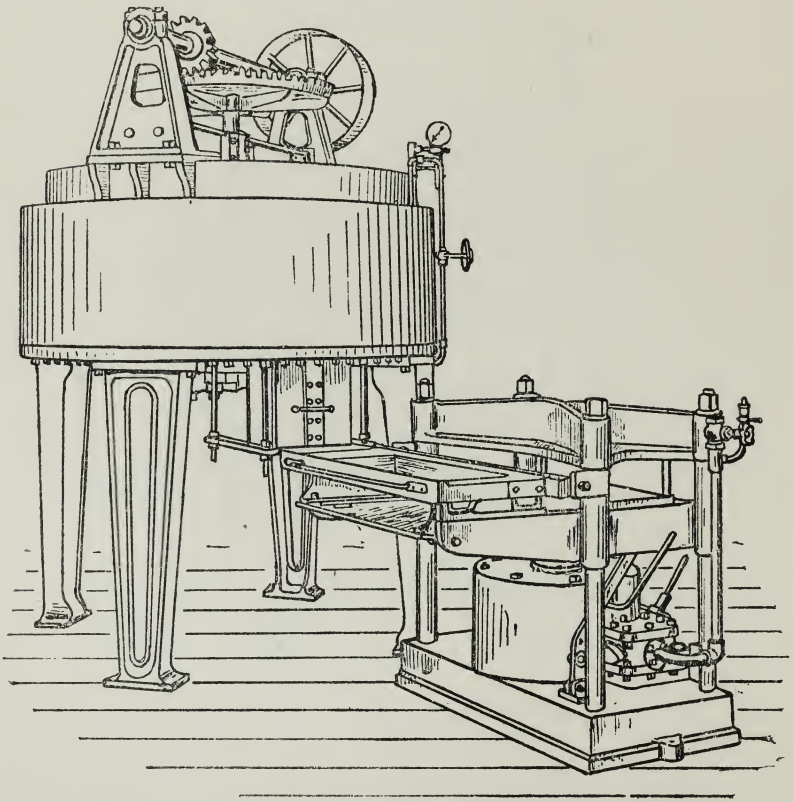


FIG. 9.—Kettle and Moulding Machine (Robert Middleton).
[Rose, Down and Thompson, Ltd., Hull.]
("The Production and Treatment of Vegetable Oils," T. W. Chalmers.)

away more freely. Heating also coagulates the albuminous matter which is retained in the press cake. Frequently a little steam is admitted direct into the kettle, not so much to heat the meal, but to improve its condition and to facilitate the flow of the oil. The time and temperature of heating may be 20 minutes and 170° F. respectively.

The meal is withdrawn from the kettle in suitable amounts and is immediately rough-moulded in a machine to the form of slabs suitable for the press in use, and as quickly as they are made the slabs are transferred to the press.

Pressing.—In the Anglo-American press the interspace between the ram and the top plate is provided with a number of iron plates (10–20), usually suspended evenly one over the other. Between the plates are placed cakes of uniform size as they come from the moulding machine. On the application of pressure the plates are forced together, thus squeezing the oil from the meal and causing its exudation through the cloths surrounding each cake.

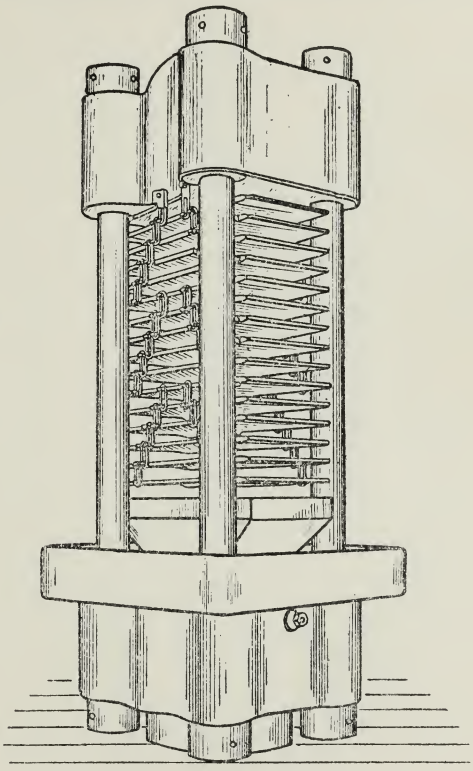


Fig. 10.—Type of Anglo-American Press. Plates supported by Links. (Rose, Down and Thompson, Ltd., Hull.)

On the release of the pressure the plates fall again into their correct position. The presses are designed for a pressure of two tons per square inch. The columns are of mild steel and the bottom has a large receptacle for the expressed oil, from which it is conducted to underground tanks. The plates may be supported by racks, or by links, as in the figures.

The press is undoubtedly efficient. It is simple, and running in conjunction with the modern meal-moulding machine, it is easily and quickly loaded. It is rapidly

unloaded, but the stripping of the press bagging from the cakes may involve considerable labour, so that special machinery may have to be installed for mechanical stripping.

The presses are best adapted for dealing with seeds containing a moderate amount of oil. The cake meal is pressed only on two sides and not round the edges. The plates are often corrugated so as to prevent, as far as possible, the meal from spreading, which is occasionally successful but not always so with seeds of high oil content. For seeds containing a high percentage oil a box-cage type of press is preferred (Chalmers, *loc. cit.*). The press cakes are the linseed cake of cattle food.

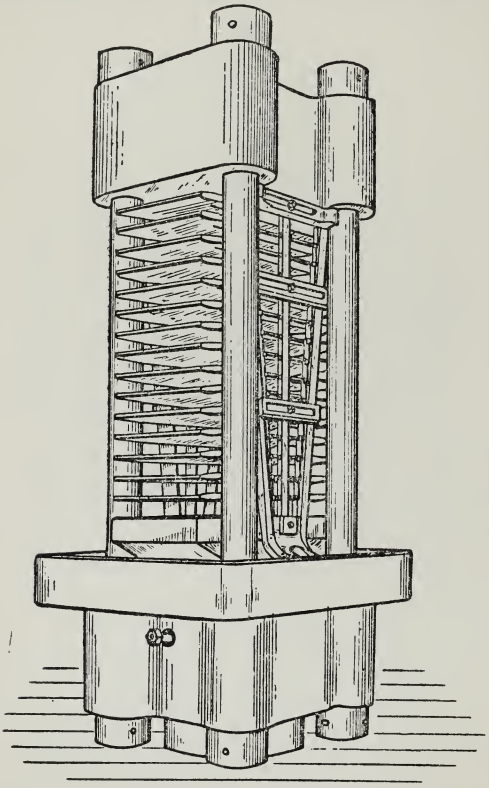


FIG. 11.—Type of Anglo-American Press. Plates supported by Racks. (Rose, Down and Thompson, Ltd., Hull.)

The Extraction Process.—The 5–10 per cent. oil left in the press cakes is not a source of loss, but the cake from which the oil has been entirely extracted can be fed direct to cattle without requiring dilution with bran and other substances, as is the case with the ordinary press cake. The oil extraction solvents must be carefully selected. Messrs. G. Scott and Sons, Ltd., London, make an oil extraction plant in which benzol is used as solvent. Benzol is stated to be one of the most difficult solvents to remove from the oil, but it is the safest and the results are considered

to be satisfactory. The extraction is performed cold. In the continuous still the descending oil and solvent are met by an ascending current of steam, so that the benzol is carried away with the steam. The working charges are very low. The coal required per ton of raw material may amount to two or three cwt. and the loss of solvent may be returned at 1½ galls. per ton of seed treated. The statement by Mastbaum (*Z. angew. Chem.*, 1916, *9*, 719), that the extracted oil dries slower than the pressed oil must be doubted. In the pressed oil it was suggested that the more fluid glycerides, *i.e.* the unsaturated glycerides, would be extracted first, but as linseed oils contain mixed glycerides such a differentiation is not possible by a pressing extraction process. For fuller details respecting the properties of linseed oil and other drying oils reference may be made to Lewkowitsch, " Oils, Fats, and Waxes," 5th edition, and to Fryer and Weston, " Oils, Fats, and Waxes," 1917.

A short description of the properties of several paint and varnish oils must be given, viz. Perilla, Soya, Poppy-seed, and China wood oil (Tung oil).

Perilla Oil is expressed from the seeds of Perilla Ocimoides (*Nankinensis*), an annual plant growing in China, Japan, and the East Indies. In Japan it is employed as an adulterant of lacquer. Very little is exported to the United Kingdom. In Manchuria it is stated to be used for edible purposes. In spite of its high iodine value (206) and high insoluble bromide value of its fatty acids, its drying power is stated to be inferior to that of linseed oil. The statement that it forms " drops " when spread on a surface is not generally accepted by users of the oil. H. A. Gardner (" Paint Researches," 1907) reports favourably on the use of perilla oil in paints and linoleum.

Soya Bean Oil.—The soya bean (*Glycine hispida*) is indigeneous to China, Manchuria, and Japan. It was practically unknown in this country before 1908, or until the Russo-Japanese war. Since that time the use of oil and cake has spread phenomenally.

Of late the demand has dropped, although the oil cake as

a cattle food is a rival to linseed and cotton cake. The oil belongs to the less active drying oils, although with driers it gives a fair drying oil (Gardner, *Circular No.* 69, Paint Manufacturers Assoc. of the U.S.A., Aug., 1919). The low iodine value (130) with an insoluble bromide value, 7·8, show that its oxygen absorbing power is small. The oil is in demand in large quantities for edible purposes, but its use in paints is limited. The beans contain 18 per cent. oil, from which 10–13 per cent. can be extracted by either native methods, or by the Anglo-American process. The emulsification of the oil with gluten or casein-like bodies in the beans is the basis of some patents for artificial milk (Melhuish, B.P. 24572 (1913), and Eng. Pat., 9626 (1915), also "B. A. Reports on Colloid Chem. and its Industrial Applications," 1918, 106). The emulsifying power of the oil seems superior to that of other drying oils.

Pararubber Seed Oil.—This oil, obtained from Para rubber seed kernels, has been investigated recently at the Imperial Institute (*Bulletin of the Imperial Institute*, 1913, vol. xi. 551). It dries less quickly than linseed oil, but it would be a valuable substitute when linseed oil is high in price. For linoleum manufacture it is considered to be unsuitable. The usual constants of the oil are : sp. gr., 15°, 0·925 ; acid value, 16·8 ; saponification value, 192·1 ; iodine value, 131–138. See also pp. 29, 30.

Poppy-seed Oil.—The seeds of the opium poppy (*Papaver somniferum*) are grown in India, Russia, France, and Asia Minor, and contain 40–50 per cent. of an oil which when cold-drawn is almost colourless (white poppy-seed oil), and possesses a pleasant taste. The cake is rich in nitrogen, and is highly prized as a cattle food. The oil is a fair drying oil and is used more in artists' colours than in ordinary paints. The seeds are generally expressed twice, the second pressing being carried out hot and yielding an inferior oil which is extensively used for soft soaps. The colourless oil is also used for adulterating olive oil.

In describing the oil obtained from any seed or nut it must be remembered that the utilization of the press cake

is a prime factor in the successful application of an oil. If the cake is useless the development of the oil is retarded. It is for this reason that attention has been drawn to the usefulness of the press cake in the description of the several oils. Poppy-seed oil is said to contain 65 per cent. linolic acid, 5 per cent. linolenic acid, and 30 per cent. oleic acid (Hazura). The iodine value is 131–157.

China Wood Oil (Tung Oil).—The seeds of *Aleurites cordata* are contained in a pod or nut about the size of a small orange containing usually about three seeds. These seeds can easily be distinguished from those of linseed by their size.

The seeds are treated by crude native methods, and the yield is 40 per cent. from an oil content of 53 per cent. The cold-pressed oil is pale and is generally exported. The hot-pressed oil is dark in colour. The oil cake is poisonous and can be used only as a fertilizer. In China it is the custom to impregnate the wood of boats with the oil, hence the name China wood oil (Seeligman).

Recently the cultivation of the tree has been undertaken in the Southern States of North America. In 1914, 40,000 trees were in cultivation and the results were satisfactory. No doubt the trouble respecting the unsuitability of the cake as a cattle food will be overcome, and the application of modern methods of crushing and refining on the spot will enhance the importance of cultivation of *Aleurites*. In 1906 nearly 29,000 tons were exported from Hankow. The literature on tung oil is very extensive ("Index to Patents, Technology and Bibliography of China Wood Oil," A. H. Stevens and J. W. Armitage). Tung oil has marked peculiarities differing from linseed oil in the following respects:—It dries in about two-thirds the time of linseed oil, giving a film which is white, dull, opaque, and crinkled. These effects are much reduced in the presence of "driers," but they are especially marked if drying be retarded in a gas-laden or foul atmosphere. The surface puckers or webs, and becomes matt with a finely radiating crystalline appearance.

Often the film may become uniformly opaque with a ground glass appearance which, when examined under the microscope, is seen to be similar to the above. If the drying is carried out at temperatures above 80° C. the film is transparent and smooth. The change may be due to formation of a solid isomer; such an isomer is produced when wood oil is exposed to light. The crystalline isomer is readily oxidized to a white solid peroxide (Morrell, *Trans. Chem. Soc.*, 1912, *101*, 2082). Another peculiarity is the rapid gelatinization of the oil. When heated to 288° C. for 9 minutes, it sets to a hard transparent jelly. This property can be used for detection of impurities in the oil, because the addition of 12 per cent. of another oil, *e.g.* soya bean oil, will retard the gelatinization at that temperature. The change is due to polymerization which differs greatly in rate from that of linseed oil.

Schumann (*J. Ind. Eng. Chem.*, 1916, *8*, 5) has put forward the view that a dipolymeride is first formed which afterwards gels. He discusses the mode of preventing the coagulation, which is a most undesirable property although the rapid formation of the dipolymeride is of great importance and its proper control has been the subject of much investigation. Careful research is gradually overcoming the difficulties due to the rapid gelatinization. The durability of the treated tung oil is generally superior to that of linseed oil, and when the defects of webbing and coagulation are overcome by the manufacturer he can produce a much improved protective coating, but skill and judgment are necessary in the treatment of the oil. Owing to the rapidity of coagulation it is very difficult under ordinary conditions to incorporate copal resins with raw wood oil in a varnish mixing.

It may be mentioned that the isomer of wood oil is the only crystalline drying oil which has been isolated in a pure condition (Morrell, *loc. cit.*).

The following table shows a comparison of the constant of linseed and China wood oils :—

	Linseed oil.	China wood oil.
Sp. gr. (15° C.)	0·933	0·9405
n	1·4831	1·5174 (12·5° C.)
D. acidity	0·4	3·3
Saponification value ..	197	192
Iodine value	185	168
Per cent. increase in weight on exposure to air ..	17·6 (8¾ days)	13·5 (8¾ days)

The importance of its metallic salts will be referred to under the theories of drying. Boiled with caustic alkalies, it yields soaps which are granular in comparison with ordinary soaps, since in the pure state the alkali salts of elaeostearic acid (C18, H32, O2), of which tung oil is the glyceride, are crystalline substances which are sparingly soluble in water. Owing to the small amount of impurity China wood oil lends itself readily to favourable investigation, the only foreign component (with the exception of the dissolved solid isomer) known at present is oleic acid to the amount of 10 per cent. (Fahrion states that 2–3 per cent. solid acids are present.) It gives no other insoluble bromide either as glyceride, or when transformed into the free acid. A solid tetrabromide of the same melting point has been obtained from the two forms of glycerides.

Its peculiar drying properties must be connected with the orientation of the double linkages in the molecule, since it is isomeric with the glyceride of linolic acid (a much slower drying oil) which is present in poppy-seed oil to the extent of about 65 per cent.

Linolic acid,

$$CH_3(CH_2)_4CH : CH.CH_2.CH : CH(CH_2)_7COOH$$

(Goldsobel, *J. Russ. Phys. Chem. Soc.*, 1906, *38*, 182).

Elaeostearic acid,

$$CH_3(CH_2)_3CH : CH[CH_2]_2.CH : CH.[CH_2]_7CO_2H$$

(Majima, *Ber.*, 1909, *42*, 674; 1912, *45*, 2730).

If proper account be taken of the peculiarities of tung oil, resin mixings containing it are superior in durability to those prepared with linseed oil, but the conditions require careful attention and neglect of them results in highly undesirable products.

Other oils in use, in small quantities, for paints and varnishes are :—

Walnut Oil.—A very pale oil used by artists, because paints made with it have a less tendency to crack than those containing linseed oil.

Japanese Wood Oil.—Obtained from *Paulownia imperialis;* it is very similar to China wood oil, but gelatinizes less readily.

Candlenut Oil, Niger Oil, Sunflower Oil, and Hempseed Oil possess drying properties whereby they may be used in paints and varnishes, but their drying properties are inferior to those of linseed oil. Provided the price of linseed oil is not much higher than that of the five oils mentioned, the demand for them is very limited and the supply is much smaller. They are used chiefly for soap making, or for edible purposes.

Among the animal drying oils menhaden, or fish oil, can be used as a drying oil. The production from *Alosa menhaden* (a fish resembling a herring) amounts to nearly half a million tons per annum, from the Atlantic coastline of North America. It is cheaper than the vegetable oils, and is used for adulterating paints or for leather cloth or oil tablecloths, in the United States. It is not popular in this country for paints and varnishes because of its odour and general inferiority to linseed oil. Toch (*J. Ind. Eng. Chem.*, 1911, *3*, 627) recommends a mixture of 75 per cent. fish oil and 25 per cent. linseed oil for outside paints, but generally its durability is inferior to linseed oil. It owes its drying powers essentially to the presence of clupanodonic acid (which gives an insoluble octobromide), but its chemical composition is not fully known. The oil content of *Alosa menhaden* is about 15 per cent.

Resin oil and pine oil will be referred to in the chapter on Resins.

Boiled, Blown, and Stand Oils (Lithographic Varnishes).—Linseed oil when heated to 220°–280° C. for several hours in contact with the air is said to have its power of absorbing oxygen increased (Hurst and Heaton, " Painters'

Colours, Oils, and Varnishes"). It is customary to add small quantities of metallic driers whereby the resulting "boiled oil" is essentially an oil containing a metallic catalyst.

The oil may be heated over a fire in large boilers holding 100–600 gallons: the boilers are made of wrought-iron plates of the form shown in Fig. 12, and the bottom, which is made separately, is riveted to the sides. The corroding action of the fire is greatest on the bottom of the boilers, which are thus replaceable. They should be set over furnaces with fireplaces outside the boiling shed. A suitable cover should be fixed on the pot to allow the ingress of air and the removal of the irritating and acid fumes from the boiling oil. The oil in the pots (not more than two-thirds full) is carefully heated up to 280° C. Great caution must be exercised at first otherwise the oil may boil over owing to the presence of water and of mucilage. After a time the oil "boils" quietly and is kept at 280° C. for not less than 2 hours. After it has been boiling for ½ hour a small quantity of driers is added from time to time. The time of boiling and the quantity of driers varies, but generally 5 lbs. per ton of oil and 5½ hours heating are adequate. The cold clear oil is drawn off as boiled oil and the foots are used for putty or mixed into cheap paints. The oil darkens in colour during the boiling due to the presence of decomposition products depending on the temperature of the operation and the nature and quantity of the driers used. Manganese dioxide produces a darker oil than litharge. Lead and manganese acetates, or manganese oxalate, produce the palest oils. The temperature of the boiling process should be kept as low as possible so as to prevent excessive darkening of the oil. The loss in weight of the oil is small, considerably under ½ per cent. even after boiling for 14 hours. The direct heating of linseed oil over a fire is being superseded by

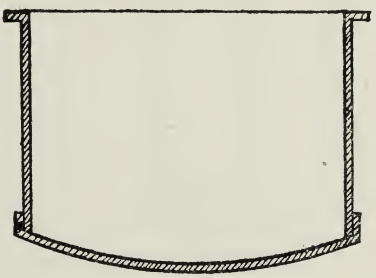


FIG. 12.—Oil-boiling Pan.

a steam process. The oil is run into a tank fitted with a closed steam coil and heated for about 2 hours at a temperature of 203°–206° C. This preliminary treatment probably assists in coagulation of the mucilage and reduces the frothing of the oil at the next stage of the process.

The hot oil is run into a steam-jacketed boiler provided with a stirrer and an air inlet as in Fig. 13. The oil is heated by the steam jacket and air is blown through it. The driers are introduced from time to time, and on completion of the process the oil is run into settling tanks (Vincent, *J. S. Arts*, 1871). The oil-boiling plant supplied by Messrs. Rose, Down and Thompson is on the same general principle, differing in mechanical details. During the boiling with driers it is evident that the incorporation of the driers provides a "drying oil." In the presence of the air oxidation undoubtedly occurs with improvement in the body and gloss of the oil. It must be pointed out that the peroxides of the more active components of linseed oil may cause oxidation and polymerization of the less unsaturated glycerides whereby thickening ensues. The small quantity of the driers assist in the production of the peroxides. The action of the driers is to shorten the slow initial oxidation as shown in the accompanying diagram.

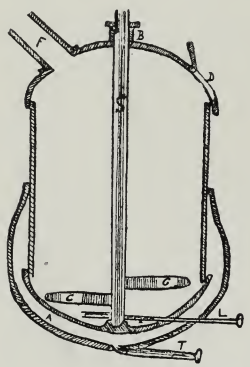


FIG. 13. — A, Steam Jacket. B, Centre for Vertical Shaft. C, Agitators. D, Oil (inlet). F, Flue. L, Air into Oil. S, Vertical Shaft. T, Steam

Boiled oil is of a brown colour of varying depth of shade. Its colour is characteristic and peculiar, different from that of linseed oil. The specific gravity varies between 0·933 and 0·952, depending on the mode of manufacture: the drying time is likewise variable from 5–20 hours. It gives a hard lustrous surface which is liable to crack on exposure to air, and is therefore mixed with raw oil so as to obtain a more elastic coat. Exposure to light is stated by some to darken the oil although linseed oil is bleached under

similar circumstances. The properties which the consumer requires for use in paint and for coating wood, masonry, and metal (generally iron) are consistency, cleanness, drying power, and freedom from added foreign impurities, *e.g.* rosin, rosin oil, mineral oil, and other vegetable oils.

It has been stated that boiled oil is essentially a linseed oil containing driers, and if this is strictly correct boiled oil might be produced by merely incorporating driers with the oil, but genuine boiled oil possess body and gloss due to oxidation and polymerization produced in its mode of treatment.

THE ABSORPTION OF OXYGEN, BY RAW, BOILED, BLOWN, AND POLYMERIZED OILS.

(Increase in Weight.)

Olive Oil (in winter time) ..	0·67% in 2 days	1·58% in 5 days	3·39% in 12 days	5·6% in 24 days
Baltic Linseed Oil (in winter time)	3·8% „ 3¾ „	13·6% „ 6¾ „	17·62 „ 8¾ (maximum)	
China Wood Oil (in winter time)		11·73% „ 6¾ „	13·46 „ 8¾ „	
East Indian Linseed Oil (in summer time)	15·9 „ 3½ „	16·3% „ 6½ „	14·2% „ 9 days	
East Indian Linseed Oil, thickened, 500–530 (32 hours) (winter time) ..	0·56 „ 3¾ „	2·0 „ 6¾ „	2·62% „ 8¾ „	10·9% in 32 days
Polymerized Oil—Stand Oil (summer)	4·9 „ 3½ „	8·9 „ 6½ „	9·6 „ 8¾ „	10·8% „ 27 „
Boiled Oil (containing lead) (summer)	14·8 „ 1 day	14·0 „ 3½ „	12·5% „ 28 „	
Boiled Oil (containing manganese and lead (summer)	15·2 „ 16 hrs.	14·6 „ 2½ „	12·8 „ 23 „	
Double Boiled Oil (summer)	16·4 „ 16 „	14·2 „ 2½ „		
Linseed Oil+2% lead manganese resinate (no heat) (winter)	14·1 „ 5 „	17·5 „ 8½ hrs. (film dry)		
Linseed Oil, blown at 100–140° C. (3 years old) (summer)	9% „ 1½ days	15·1 „ 2½ days	13·7% in 4½ days	
Cold Blown Linseed Oil (Calcutta) Pb (summer) ..	2·2% „ 3½ „	11·5% „ 5 „	16·7 „ 8 „	(film dry)
Cold Blown Linseed Oil with 2% Mn resinate (winter)	12·8 „ 5 hrs.	16·7% „ 8½ hrs.	17·1 „ 1 day	17·6 in 1½ days (film dry)
Blown at 150° C. ditto, with 2% Mn resinate (winter)	14·5 „ „	16·5 „ „	16·5 „ „	17·6 in 1½ days (film dry)
Linseed Oil heated to 280° C. and 2% Pb. Mn. resinate added	15·3 „ „	17·4 „ „	17·4 „ „ (film dry)	17·4 „ 5 days

Cf. Andés' " Drying and Boiled Oils." 1901.

From the figures in the table it will be evident that the gain in weight and the rate of drying is increased if air is blown into the oil during the heating, whereas it has little influence on the cold oil. The gain in weight is dependent on many factors, viz. temperature and general atmospheric

conditions, and is a balance between the true gain and the loss in weight due to the escape of volatile oxidation products. The viscosity of the oil is increased during the blowing process and the unsaturated acids will have undergone extensive oxidation to give glycerides from which acids can be obtained insoluble in light petroleum (Fahrion has shown that the oxidized unsaturated acids are insoluble in low boiling-point petroleum). With reference to the durability of coatings produced from boiled oils there would appear to be differences of opinion (Ingle and Woodmansey, *J. S. C. I.*, 1918, *38*, 103). If in the oxidation a high proportion of peroxide glycerides is left in the oil it is to be expected that the superoxidized oil of Reid (*J. Soc. Arts*, 1891, *39*, 398) would predominate to the detriment of the durability, but if an oxide stage be attained durability would be expected. The oxidized oil produced by blowing with a high percentage of peroxides is decomposed by lengthy exposure with the formation of liquid acidic compounds (Ingle and Woodmansey, *loc. cit.*). The conditions of blowing oils must be carefully controlled because rapidity of surface drying is not the only requisite, but the linoxyn layer must extend throughout the mass of the oil, which would be attained on the assumption that the peroxide autocatalyst was reduced to the oxide stage $AO_2+A=AO+O$. (A is the oil glyceride.)

Such oxides are most probably polymerized or they may undergo transformation into ketones of the formula [X—CH_2—CO—Y], although there is as yet no definite experimental proof of such a change. The peroxides as such may undergo decomposition into resinified aldehydic glycerides and volatile products or be transformed into hydroxyketones X—CO—CHOH—Y (Ingle, *J. S. C. I.*, 1913, *32*), but of this last change there is no definite experimental confirmation. The view of the polymerization of the products of oxidation tending to durability is supported by the fact that the permanency of polymerized oil is superior to that of an oxidized in a paint vehicle.

Lithographic Varnishes and Stand Oil.—There

would seem to be some confusion as to the exact meaning of the term "stand oil." Hurst and Heaton ("Painters' Colours and Varnishes") state that when linseed oil is maintained at a high temperature for some time in the presence of air, but without driers, it slowly polymerizes, thickening to a viscous substance of the consistency of honey and consisting largely of linoxyn. Andés considers stand oil to be a linseed oil thickened by heat or by superheated steam and a current of air. A. C. Wright ("Analysis of Oils," 1903) states that it is identical with lithographic varnishes. Extremely thick stand oil is called printer's varnish in English; as a painter's material this oil finds no application. From a summary of the authorities it is advisable to consider stand oil as linseed oil polymerized by heat without driers and without "blowing" (*Oil and Colour Trades Journal*, 1913), ("Stand Oil").

When linseed oil is heated out of contact with air polymerization ensues with a rise in the molecular weight of the oil (Morrell, *J. S. C. I.*, 1915, *36*, 105). The following table illustrates the course of polymerization in linseed oil heated out of contact of air (de Waele). The oil (Baltic oil) was heated in an atmosphere of carbon dioxide at 250° C.

	Raw oil.	12 hrs.	56 hrs.	77 hrs. (solid).
Sp. gr. 15·5° C.	0·9351	0·9423	0·9664	—
n_D., 25° C.	1·4808	1·4835	1·4936	1·4790
Iodine Value	196·6	175·2	119·8	—
Oxidized acids %	0·78	0·29	0·5	3·24
Saponification Value ..	—	—	190·7	186·0
Solid acids *	5·25	7·03	—	48·8
Iodine Value of solid acids	17·5	—	—	86·4

There was a notable increase in the proportion of "solid acids"; they were, however, transparent and of a gummy consistency. By boiling the solid product with amyl alcohol, de Waele obtained an extremely tough insoluble residue which had an iodine value of 94 and was very resistant to the action of alkalies. This observer believes it to be a closed chain compound and proposes for it the name of "cyclolin." (Lewkowitsch, "Oils, Fats and Waxes," 5th ed., Vol. 3, p. 125.)

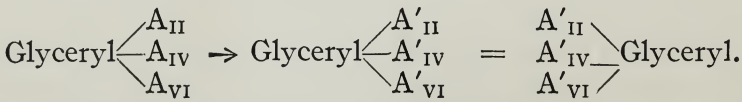
* Fachini and Dorta's acetone method.

Morrell has found (*loc. cit.*) that linseed oil thickened at 260° C. for 28–60 hours contained 50 per cent. of an oil of high molecular weight insoluble in acetone. An examination of the two portions showed that, in addition to polymerization, there was strong indication of alteration in the position of the double linkages of the mixed glycerides of which the oil is composed. The most unsaturated acids are polymerized first. The polymerized glycerides on being transformed into the methyl-esters by sodium methylate yield monomolecular esters of acids which are not identical with the normal acids in the oil glycerides. The drying power of the polymerized oil is much slower than that of linseed oil and the viscosity varies according to the conditions of heating. Leeds (*J. S. C. I.*, 1894) gives the results of the examination of a number of lithographic varnishes.

	S.G. at 15° C.	S.V.	I.V.	Oxidized acids.	Hexabromides
Raw linseed oil	0·9321	194·8	169·0	0·3 %	24·17 %
Tint varnish	0·9584	197·5	113·0	1·5 %	—
Thin varnish	0·9661	196·9	100·0	2·5 %	2·0
Middle varnish	0·9721	197·5	91·0	4·2	0·95
Strong varnish	0·9741	190·9	86·0	6·5	—
Burnt thin varnish ..	0·9675	195·5	92·7	0·85	0·0

(Burnt thin varnish is obtained by heating the oil to its flash point and allowing it to burn quietly with constant stirring).

From the above figures it is evident that polymerization has occurred which may be expressed by the following scheme, roughly indicating the changes in the orientation of the linkages of the unsaturated carbon atoms.



A_{II} and A'_{II} = oleic acids
A_{IV} and A'_{IV} = linolic acids
A_{VI} and A'_{VI} = linolenic acids

The incorporation of thickened linseed and other oils into varnishes and paints gives a coating of improved protective power against corrosion (M. Toch, *J. S. C. I.*, 1915, *34*, 592), and Friend has shown that polymerized oils in paints used on iron have the same property. The formation of ring

complexes consequent on polymerization presumably retard the breaking down of peroxides or oxides of the glycerides on exposure to atmospheric agents.

Theories of Driers.—The drying of oils is greatly accelerated by the presence of small quantities of metals, metallic oxides, and salts, *e.g.* linseed oil which ordinarily takes 3 days to dry will dry in 5–8 hours in the presence of 5 per cent. of dissolved lead. Many other metals show a similar accelerating action. Fokin (*Seifen. Zeit.*, *34*, 821) places metals in the order given in the list :—

Co, Mn, Cr, Ni, Fe, Pt, Pd, Pb, Ca, Ba, Bi, Hg, U, Zn.

He states that the velocity of drying increases with the cube root of the concentration of the catalyst ; a statement which must be received with caution because drying is not solely oxidation. Lippert (*Zeitsch. angew. Chem.*, 1898, *11*, 412), Weger (*Chem. Rev. Fett. u. Harz. Ind.*, 1899, *4*, 301), and Kissling (*Z. angew. Chem.*, 1891, *4*, 395) showed that the "drying" was virtually a process of autoxidation and that linseed oil could absorb or combine with more than 20 per cent. of its weight of oxygen. The term "autoxidation" is given to those processes of combustion in oxygen or air which take place at the ordinary temperature and proceed with a slow but measurable velocity. The reaction velocity of the oxidation of linseed oil was examined by Genthe (*loc. cit.*) who found that the increase of weight-time curve showed the sinuous character of an autocatalytic reaction (Figs. 14 and 15). From the nature of this curve it must be assumed that some intermediary product is formed which exerts a catalytic function on the oxidation of the oil. This intermediary is a peroxide (Engler and Weissberg, *Chem. Zeit.*, 1903, *27*, 1196). The formation of the intermediary is accelerated by light (Genthe, *loc. cit.*). An equation corresponding with the curves obtained by Genthe is of the following form :—

$$dx/dt = K(a-x)(b+x)$$

a and b are the initial concentrations of linseed oil and the

autocatalyst and x is the amount of linseed oil oxidized; therefore a quantitative relationship must exist between the linseed oil oxidized and the autocatalyst generated.

Mackey and Ingle (*J. S. C. I.*, 1917, *36*, 319) classify metals in the following order of descending powers of drying :—

Co, Mn, Ce, Pb, Cr, Fe, U, Na, Ag, Zn, Hg, and Al.

The method employed is novel: cotton wool soaked in

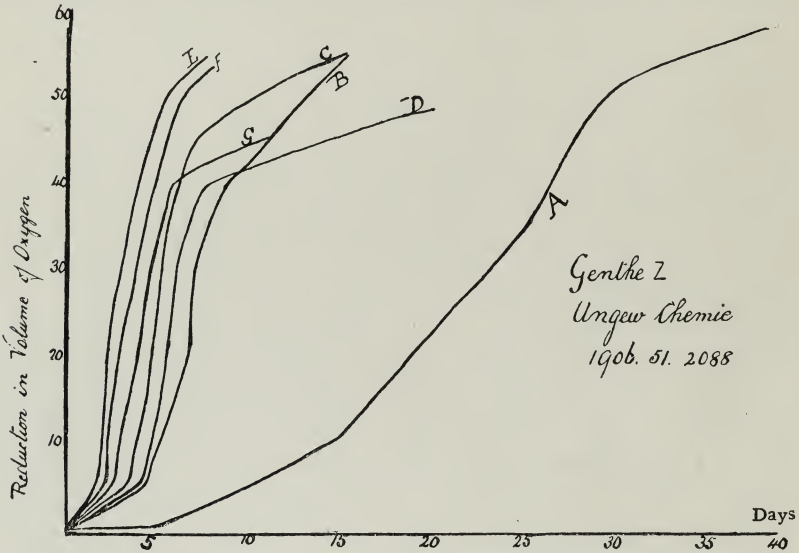


FIG. 14.—Oxygen Absorption of Oils.

A. Linseed Oil
B. ,, ,, +1 % Lead Resinate
C. ,, ,, +1 % Manganese Oleate } In the dark.
D. ,, ,, +1 % Benzoyl Peroxide
E. ,, ,, Blown
F. ,, ,, +1 % Lead Oleate } In diffused daylight.
G. ,, ,, Previously exposed to light from mercury lamp.

linseed oil containing the metal to be classified was placed in a cloth oil-tester (*J. S. C. I.*, 1896, *16*, 40) and the time taken to attain a temperature of 200° C. was noted. The great rise in temperature during the oxidation and drying of an oil shows the importance of preventing the accumulation of oiled waste rag in a factory where vegetable oils are used. The usual method of testing of drying power is that of the craftsman who fixes the time when the film becomes satisfactorily dry to his finger, which condition is preceded by a

"*dust dry*" period (Davidson, "The Setting Value of Linseed Oil," *Proc. P. and V. Soc.*). Rough though the method is, with a personal error of half an hour and a dependence on temperature and atmospheric conditions, it is satisfactory for practical purposes in the hand of a skilled worker. The results in the gain-in-weight trials on oxidation are to be considered as deciding broadly between drying and semi-drying oils or between metal and metal as "driers," but in practice the rate of oxidation is not sufficient to establish the superiority of any metal.

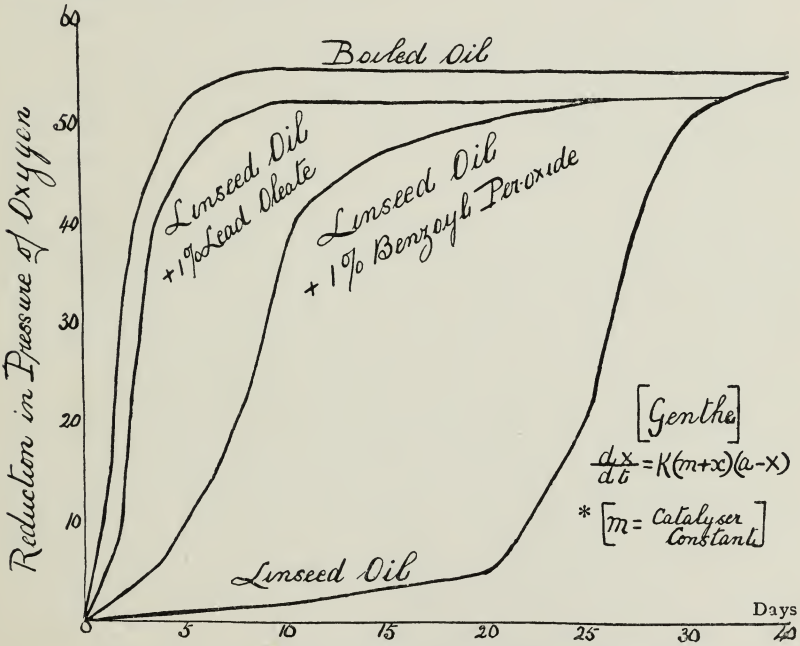


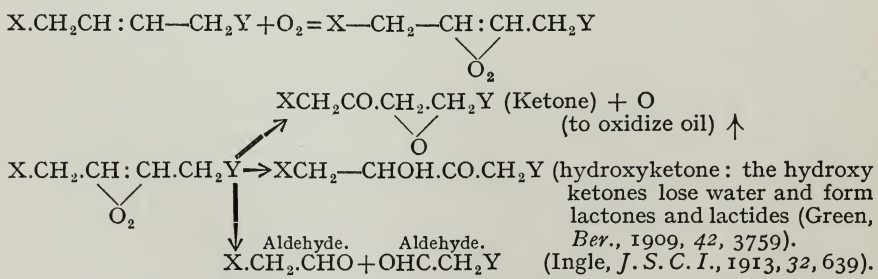
FIG. 15.—The Drying of Linseed Oil (diffused daylight.)

Manganese is considered by Ingle to be less satisfactory than lead, although its oxidizing power is greater, and his opinion has much to recommend it from general practice. From the lists given above it is evident that a metal, which can form more than one oxide, acts as a drier or oxygen carrier when it is in an oil-soluble form, provided that the salts of the lower oxides are more stable than the salts of the

* *m* is a constant which is proportional to the initial concentration of the auto-catalyser present.

higher oxides. It has been stated that the more oxides a metal can form the greater will be its catalytic activity. The metallic driers are catalysts, and the term catalysis as defined by Henderson ("Catalysis in Industrial Chemistry," 1919) is more generally used to designate those chemical changes of which the progress is modified by the presence of a foreign substance: the agent which produces the effect is called a catalyst. The theories advanced to explain the mechanism of catalysts fall into two classes: (*a*) chemical and (*b*) physical.

The chemical theories of drying depending on the formation and decomposition of unstable intermediate products are the most favoured, although the importance of the physical aspect is growing. On Engler's hypothesis of catalytic oxidation (*Ber.*, 1897, *30*, 1669), oxygen (actor) oxidizes the metal of the drier (inductor), which in turn oxidizes the oil (acceptor). In the description of the general properties of linseed oil it was pointed out that molecular oxygen was absorbed at the double linkages with the formation of peroxides. The peroxides are components of "linoxyn," the oxidized skin of the oil. It was pointed out that these peroxides may undergo transformation into oxides or yield ketones or hydroxyketones (Fahrion, *loc. cit.*); moreover, the molecule may be ruptured in the presence of hydrolytic agents to yield acids and aldehydes (probably polymerized with aldol condensation) after the fashion of the decomposition of ozonides described by Harries and others.


X.CH2CH:CH—CH2Y + O2 = X—CH2—CH:CH.CH2Y
O2
XCH2CO.CH2.CH2Y (Ketone) + O
(to oxidize oil)
O
X.CH2.CH:CH.CH2Y → XCH2—CHOH.CO.CH2Y (hydroxyketone: the hydroxy ketones lose water and form lactones and lactides (Green, Ber., 1909, 42, 3759).
O2
Aldehyde. Aldehyde.
X.CH2.CHO + OHC.CH2Y (Ingle, J. S. C. I., 1913, 32, 639).

From the above it is evident that the peroxide will not be the final product of the oxidation of linseed oil, and from Genthe's curve with its equation the intermediate peroxide

is only a stage in the drying process. From an investigation of the action of cerium salts on Chinese wood oil (Morrell, *J. Chem. Soc.*, 1918, *113*, 111) it is evident that only half the amount of oxygen is taken up by the oil as would be expected from the number of double linkages and that it is only after long exposure to oxygen that cerium tungate absorbs an amount of oxygen corresponding to the peroxidation of all the double linkages. The acid isolated was a peroxide which slowly polymerized.

$$\mathrm{XCH:CH.Z{-}CH:CH.Y + O_2 = X.CH:CH{-}Z.CH.CH.Y}$$

$$\rightarrow \mathrm{X.CH.CH{-}Z.CH.CH.Y}$$

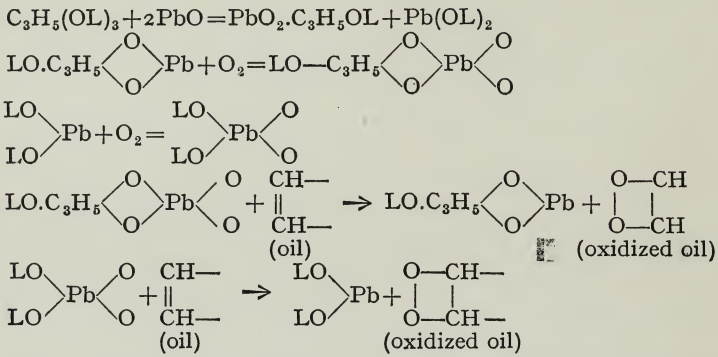
$$\mathrm{X.CH.CH{-}Z.CH.CH.Y}$$

It is possible that cobalt and manganese may produce superoxidized oil in which all the double linkages are attacked, and such a condition would not favour durability because of the possibility of degradation into simpler molecules.

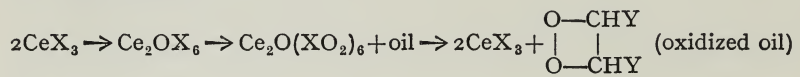
It must be again pointed out that the oxygen absorption is not the only measure of the drying qualities of an oil as instanced by the inferiority of drying of the ethyl esters of linseed oil or the free acids or the ethyl ester of β-elaeostearic acid (from tung oil) (Morrell, *J. Chem. Soc.*, 1912, *101*, 2082) compared with their respective glycerides. The glyceryl radicle probably plays a part in the setting, oxidation the polymerization. To return to the function of the metal: the metallic elements act as oxygen carriers or as pseudocatalysers serving to stabilize or assist in the formation of the autocatalytic peroxide, and very small amounts are able to produce the drying of large quantities of oil. Many theories have been put forward to explain the action of the metal and much work has been done by many investigators, but none are entirely satisfactory owing to the

Note.—It has been found that the percentage of linoxyn in an oil film is higher if the oil has been previously polymerized by heat.—(R. S. M.)

difficulty of investigating the products of the reaction. Ingle (*J. S. C. I.*, 1917, *37*, 319), after reviewing earlier work on the subject, holds the view that in boiled oil litharge and linseed oil react to form glyceryl plumbolinolenate and linolate (there is general agreement that the glyceryl radicle is unacted on in the drying process).



In the oxidation of cerium tungate (Morrell, *loc. cit.*) the process of oxidation of the salt was shown to be represented by the scheme :—



The cerous salt changes first to ceric salt which facilitates the formation of peroxides of the acid.

The form in which the catalysts are used varies with the requirements, but finely divided metals (except iron) are very rarely used. (Livache, *Compt. Rend.*, 1883, *96*, 250 and *102*, 1169.)

The metallic oxides and salts, especially of the drying oils, acids, and resinates, are generally employed. The most important inorganic driers are litharge, red lead, and lead borate or the oxides, borate or sulphate of manganese. Among the salts of organic acids are the "linoleates" of lead, cobalt, and manganese, lead acetate and manganese oxalate. Iron in the free state or in Prussian blue is used in the patent leather industry.

The physical theory of catalysis seeks to explain the phenomena as due to the condensation or increase in

concentration of the reacting substances at the surface of the catalyst, such increase in concentration being due to the action of capillary forces (Henderson, "Industrial Catalysis," 1919). This aspect has been neglected in the consideration of paint and varnish drying problems (*British Association Reports*, 1920). The influence of surface phenomena is of great importance and the activity of the metallic driers is due partly to chemical and physical causes. For a discussion of the rival theories reference may be made to Mellor's "Chemical Statics and Dynamics"; and Lewis, "A System of Physical Chemistry," Vol. 1; also E. Rideal, "Catalysis in Theory and Practice," 1919.* It must be remembered that substances of a colloid nature are under consideration in paints, varnishes, and oils, and the activity of metals in solutions containing colloids is more active than in aqueous solutions. If the surface tension to air of a lead drying oil is lower than that of the oil (there is reason to believe that this is so) the surface concentration of the lead would be increased. A more careful study of Livache's method by drying in the presence of finely divided lead would establish a connection with the phenomena observed when unsaturated oils are reduced with hydrogen in the presence of metallic catalysts. It is for the chemist to decide from the examination of the products of oxidation the chemical changes which have occurred. It would appear that the activity of driers is to be attributed to causes put forward by both theories taken together.

Methods of Testing the Commoner Drying Oils.—It is impossible to go into the details of the testing of the commoner drying oils in this general review of their properties. Reference must be made to the many text-books on the subject. A few English publications may be mentioned.

Lewkowitsch, "Oils, Fats, and Waxes," 5th edition. Macmillan.

Fryer and Weston, "Oils, Fats, and Waxes." Camb. Univ. Press. 1917.

* Morrell, "Catalysis applied to the Oxidation of Oils," *J. S. C. I.*, 1920, *39*, 153T.

Ingle, "Oils, Resins, and Paints." Griffin. 1915.

A. C. Wright, "Analysis of Oils." Crosby Lockwood. 1903.

The most recent account and fullest in detail is given in Fryer and Weston's work, Part 2, to which the reader must be referred. Only those methods which concern drying oils will be indicated here. Usually it is advisable to determine :—

(1) Specific gravity at 15·5 C.

(2) Iodine value.

(3) Saponification value.

(4) Acid value.

(5) Insoluble bromide value of the oils or their corresponding acids.

(6) The drying times of the oil against a standard linseed oil.

(1) *Specific Gravity.*—With the exception of tung oil (0·940), all the drying oils have a specific gravity between 0·925 and 0·933.

(2) *Iodine Value.*—This is a valuable guide as to the nature of the oil as will be evident from the following figures :—

Perilla oil : 205–206.

Linseed oil : 170–200.

Tung oil : 160–170, distinctive odour; somewhat unpleasant.

Candlenut oil : 164.

Hemp oil : 148, oil generally of a greenish colour.

Walnut oil : 140–150, characteristic odour of walnuts.

Poppy oil : 130–140.

Soya bean oil : 128–135, a slight distinctive odour and high content of saturated acids, (13–15 per cent.), (de Waele).

Pararubber seed oil : 138.

Sunflower oil : 125–133.

Menhaden oil : 160–182, fishy odour. Fish oils are especially recognized by the insolubility of their brominated products in a mixture of acetic acid and carbon tetrachloride.

If the oil is a raw oil, adulteration with non-drying oils would be indicated by the iodine value, but a polymerized linseed oil would give values much lower, so that other tests are necessary.

(3) *Saponification Value.*—This is generally 186–196. A low saponification value would indicate adulteration with petroleum, rosin oil, and even rosin.

(4) *Acid Value.*—This is for most oils, 0–2. Generally the acid value is a guide as to the grade of an oil and the care taken in its extraction. Polymerized oils have a higher acidity and the presence of rosin raises the value considerably.

(5) *The Insoluble Bromide Value.*—This is an important determination often overlooked because of the time required in carrying it out. The principle is the estimation of the ether-insoluble bromides obtained from the oil acids or glycerides. From the values it is possible to form a fair idea of the proportion of linseed or menhaden oil present in a mixture. Tung oil gives no ether insoluble bromides nor do the lithographic oils. Linseed oil gives 32–38 per cent.; candlenut oil, 11·0; menhaden oil, 63–64. (Steele and Washburn, *J. Ind Eng. Chem.*, 1902, *12*, 52.)

(6) *Time of Drying.*—The drying times of a lead-manganese drying oil against a similar drying oil made from linseed oil is a necessary test to be made. The nature of the film is of importance.

The solidification test for tung oil (Browne's test) is the quickest way of characterizing the oil, because the presence of 5–10 per cent. of foreign oils can be detected by its means. The principle of the method is the coagulation at 282° C. in 12 minutes of a small quantity of the oil which, when solid at that temperature, will show a clean cut when stabbed with a steel spatula.

It is advisable to test oils for added rosin or rosin in the form of resinates which improve the drying. It can be detected by the Liebermann-Storch Reaction (Fryer and Weston, Part 2, 222). A high acidity would indicate free rosin added, otherwise the presence of rosin is due to metallic resinates which can be detected by examination of the ash.

For details as to Linseed Oil Standards reference must be made to: "Some Technical Methods of Testing Linseed Oil,"

* *Analyst*, 1912, *37*, 410.

Bureau of Standards, Washington, U.S.A., 1916, page 11; "Reports of the American Society for Testing Materials," 1915, 417–427.

There are for each oil characteristic properties, for the details of which references must be made to the authorities quoted. Sufficient has been given to decide whether the oil is a genuine oil by its sp. gr. and saponification value: a genuine drying oil can be recognized by the iodine value and drying time as well as the methods of detection of the common adulterants, *e.g.* rosin and petroleum. To prove the presence of foreign oils, which may be suspected, it will be sufficient to carry out the six main classes of operations outlined and to apply from the information gained the characteristic tests given under the individual oils. The difficulty of estimating the thickened oils in a mixture, especially wood oil, has up to the present not been entirely overcome, although thickened oils are only partially soluble (50 per cent.) in acetone, and a very fair conclusion can be drawn by that method of separation (Morrell, *J. S. C. I.*, 1915, *34*, 105). Tung oil may be detected in the absence of rosin, turpentine, and oxidized oils, by giving a port wine colour with iodine monochloride (Wijs' method) due to the liberation of iodine consequent on the formation of HCl by the action ICl on the oil.

Part III.—RESINS AND PITCHES

Resins

The resins are essentially of vegetable origin, being exudations of trees of many different genera and species. It is only recently that artificial resins derived from coal tar products, *e.g.* Bakelite, Cumarone, and Paraindene resins, have been used as substitutes, although for oil varnishes the natural resins are still preferred.

Commercially the resins belong to the class of gums which are for the most part produced as exudations of trees. The gums, when incorporated with liquids, form more or less viscous fluids which on drying give films of varying protective character. They all show the properties of colloids, usually forming emulsoid solutions with water, oil or other media. Some are completely soluble in water, others swell up to give jellies, whilst others are unacted on. The colloid properties of gums are in many respects similar to those of glue or gelatin, which is a typical colloid containing nitrogen, and is of animal origin. The "resins" can be readily distinguished from the true "gums" by the following simple methods :—

(1) When a resin is held in a flame it takes fire and burns with a smoky flame giving off an aromatic odour. A gum similarly treated chars and smells of burnt sugar.

(2) A resin placed in water is unaltered, whereas a gum dissolves or forms a jelly.

(3) When a resin is allowed to stand in methylated spirit or in turpentine it disintegrates and dissolves either partially or completely. A true gum is unacted on by these solvents.

("Selected Reports from the Scientific and Technical Department of the Imperial Institute," Part 3, Gums and Resins, No. 63, 1909.)

Although only the resins are the important ingredients of varnishes a passing reference to several of the true gums is advisable.

Gum Arabic is obtained from varieties of acacia and is known in the trade under many forms, *e.g.* Turkey, White, Sennar, Kurachee, Mogador, Wattle, and Senegal. These forms are all more or less soluble in water and swell up in that medium. They are insoluble in alcohol and on boiling with dilute sulphuric acid give a sugar (pentose or hexose), thus showing their carbohydrate nature. The best qualities are used for pharmaceutical, confectionery, and other purposes, whilst the commoner qualities are in demand in textile industries, as a binding material for artists' water-colours and for mucilages.

Gum Tragacanth is obtained from various species of Astragalus, indigenous to Greece, Asia Minor, Syria, and Persia. The gum flows freely from the stems when they are wounded. It is softer than acacia and cherry gums. Like gum arabic it gives a viscous fluid with water and is hydrolysed by dilute sulphuric acid to yield sugars. It is used as a thickener in calico printing and as a vehicle in many pharmaceutical preparations.

Reference must be made to the **Balsams** which are solutions or emulsions of resins in oil esters, *e.g.* esters of cinnamic or benzoic acids. The well-known Canada balsam contains 18 per cent. of oil esters, and Copaiva balsam contains as much as 60 per cent. oil esters. Other important balsams are Peru balsam and Mecca balsam. The balsams may be thick or thin fluids possessing usually a characteristic odour.

The **Resins** are exudations of trees (the vegetable origin of lac is disputed). The majority are used in varnish making. About five-sevenths of the total imports of varnish gums or resins into the United Kingdom are obtained from Imperial sources. In 1908 the imports into the United Kingdom were

valued at £2,803,535; they included shellac from India, kauri from New Zealand, copal from British West Africa, animi from Zanzibar, and dammar and copal from Singapore. Most of the Zanzibar animi is collected in German East Africa and a large part of the Singapore copal comes from the Dutch East India possessions. The resins are more or less hard (elemi is soft), friable or brittle, transparent or lustrous.

They are insoluble in water; some are soluble in alcohol, ether, or benzol; others require strong fusion before they can be incorporated with solvents used in varnish making. The researches of Tschirch and his pupils have thrown light on the composition of the resins, but a fuller investigation is necessary and a careful comparison of the components and of the decomposition products is very desirable. Generally the resins contain acids ("Resinolic Acids," Tschirch), *e.g.* rosin (colophony) contains abietic acid, amber contains succinoabietic acid from which succinic acid can be isolated; dammar yields dammarolic acid $C_{56}H_{80}O_8$; Zanzibar copal contains trachylolic acid $C_{56}H_{88}O_8$. Some acids are monobasic, others dibasic.

An important component are the resenes (Tschirch), which are oxygenated bodies, neither alcohols, esters, nor aldehydes. They are insoluble in alkalies and their inertness renders their presence in resins of great importance for varnish making. It has been suggested that the resene content is of value in estimating the quality of a varnish gum.

Elemi contains elemic acid $C_{35}H_{46}O_4$, and amyrin resene $C_{25}H_{42}O$.

Dammar contains dammarolic acid $C_{56}H_{80}O_8$, and α-resene $C_{11}H_{17}O$, β-resene $C_{31}H_{52}O$.

Mastic contains an acid $C_{20}H_{32}O_2$, and masticin resene $C_{20}H_{32}O$.

Lac contains an acid, aleuritinic acid ($C_{13}H_{26}O_4$), and a resene.

From the resin esters (resines), resin alcohols (resinols and resinotannols) have been isolated by Tschirch and his collaborators.

Amber contains a succinoresinol $C_{12}H_{20}O$: m.p. 275° C.
Pine resin contains a pinoresinol $C_{10}H_{18}O_6$: m.p. 80–90° C.
Elemi contains α and β-amyrin $C_{30}H_{49}OH$.
Lac contains resinotannol ester of aleuritinic acid $C_{13}H_{26}O_4$.
Sumatra benzoin contains sumaresinotannol $C_{18}H_{19}O_3(OH)$ (which yields picric acid with nitric acid and pyrocatechuic acid on alkali fusion).

From Tschirch's investigation it is evident that the resins contain resinolic acids, resin esters, and resenes.

The most important characteristics of the resins are colour, hardness, lustre, and specific gravity. Some resins, *e.g.* mastic, occur in droplike pieces as the resin flows from the tree, others in short cylindrical pieces agglomerated together as in sandarac, and yet others in large irregular-shaped masses as copal gums. Lac may appear in stick form from the twig on which it has been produced by the lac insect. In the trade the resins often appear in artificial forms due to previous treatment in the country of the source, *e.g.* shellac in thin plates, dragon's blood in sticks. The surface of a resin is often characteristic. Weathering of the surface produces a goose skin appearance as shown in Zanzibar copal.

According to Wiesner ("Die Rohstoffe des Pflanzenreiches") not one of the resins from plants is a chemical individual but a complex mixture. Mastic, sandarac, and dammar appear to be homogeneous : crystals are sometimes found in a matrix of resin as in elemi and Fichtenharz. The fracture of the gums is characteristic and conchoidal, sometimes lustrous or dull, *e.g.* Zanzibar copal shows dull and lustrous alternations. Benzoin, yellow accroides and others show almond structure with agglomerates of coarsely rounded masses.

The colour is very varied : from colourless to the red of dragon's blood, the yellow of gamboge, and the black of some varieties of rosin (colophonium). Generally the colour is yellow to brown. The lustre is vitreous, but it may be waxy as in the so-called almonds of benzoin. Some copals are entirely lustreless.

The most important characteristics are hardness, fusibility, and solubility in solvents.

Hardness.—According to Wiesner (*loc. cit.*) the hardness of the copal resins lies between gypsum and rocksalt; only the best copals are harder than rocksalt and a few, *e.g.* elemi, are so soft that they can be worked in the fingers. The softer varieties have low melting points; Siam benzoin melts at 75° C., whilst the hardest copals (Zanzibar) do not melt below 360° C. Generally the less fusible gums give the hardest coatings. Shellac gives a hard coherent layer whilst the fusible colophonium is easily rubbed up by the finger. In hardness and fusibility there is a wide range.

The solubility is important in deciding the uses of the resin: some resins are readily soluble in methylated spirit and are used for spirit varnishes, viz. shellac, sandarac, colophonium, and the softer varieties of copals. Others such as dammar and mastic are soluble in turpentine. Ether, benzol, and acetone are solvents for a number of resins. Copals are generally insoluble in vegetable oils until they are fused, but they will dissolve easily in the acids obtained from drying oils and in the drying oils themselves after the resins have been "run." In petroleum ether they are insoluble or sparingly soluble. (Compare Table of Solubilities, p. 87.)

The Formation of Resins in the Plant.—The resin secretion cells of a plant may be stimulated by wounding to give a flow; even if the plants show no such secretion cells normally, these cells can be generated, as in liquidambar, styrax and benzoin, by destroying the new wood, whereby the flow of balsam can be continued for years if the wound is enlarged from time to time. (Tschirch, "Harze u. Harzbehalter"; Wiesner, "Die Rohstoffe des Pfanzenreiches"; Livache and McIntosh, "The Manufacture of Varnishes," Vols. 2 and 3; Dieterich, "Analyse der Harze.")

Tschirch favours the view that lac is a secretion from the lac insect and not a direct exudation of a tree caused by the insect. It is evident that the production of resins is akin to that of the rubber latex referred to in Part I. of this volume. It is chiefly in connection with the oleoresin from species

of pine that the production of resin has been systematically studied. The output of turpentine resin is large compared with other resins. Many forms of copal are of fossil origin, whilst the softer copals from living trees are collected by aborigines, and little attention is paid to improving the yield or extending the cultivation of the parent tree.

Classification of the Resins.—In view of the complexity of chemical composition of the resins and in spite of the investigations of Tschirch and his pupils, it is difficult to classify them so that differences in chemical composition will go hand in hand with their properties which are of industrial importance. Dieterich proposes the following classification :—

(1) Resins which are esters of the aromatic series, either containing free acids or not, *e.g.* benzoin, dragon's blood, accroides. These resins are soluble in methylated spirit.

(2) Resins which are esters of special resin acids with or without free resin acids : turpentine oleoresin, mastic, elemi. These are soluble or partly soluble in methylated spirit or soluble in organic solvents.

(3) Resins which are free acids containing resenes, *e.g.* copals, dammar, sandarac, and colophonium.

For practical purposes the scheme adopted in Hurst's text-book (2nd edition) is more useful, viz. :—

(*a*) Oil varnish resins, (*b*) spirit varnish resins, (*c*) resins soluble in special organic solvents.

Unfortunately there is considerable overlapping in this simple classification. In the first class appear the copals, which are recent or fossil resins produced in prehistoric forests or dug from the soil in what is still a forest region.

The changes which have occurred in the secreted or exuded gums are not understood. Undoubtedly there has been a reduction in acidity : with polymerization, or coagulation, oxidation has occurred (the resenes are inactive oxides), but moreover with such a mixture of components in a colloid complex it is unwise to speculate. The recent copals, including manila, pontianak, etc., are not in demand by the makers of high-class oil varnishes, but their softer varieties

are soluble in methylated spirit. Rosin (colophonium) is often a component of cheap oil varnishes when rosin is cheaper than copal, and especially in varnishes containing China wood oil. In the class of oil varnish resins amber must be mentioned, although it is no longer used because of its price. Tschirch and de Jong (*Arch. Pharm.*, 1915, *253*, 290) state that the main component of amber (succinite) is succinoresene, which is the cause of its resistance to the action of reagents. Amber contains two acids, succinoxyabietic acid $C_{19}H_{29}O_2COOH$ and succinoabietic acid $C_{39}H_{59}COOH$.

The second class includes the methylated spirit soluble resins, lac, sandarac, mastic, manila copals, rosin, and accroides. These are used for coatings, giving lustrous films of rather a brittle character and slight durability for outside wear. Lac is undoubtedly the most valuable of its class, although mastic is prized as a picture varnish ("megilp") when dissolved in a suitable solvent.

The third class included many of the second in addition to dammar and the oil varnish resins which have been fused or "run." The solvents employed may be turpentine, benzol, acetone, or coal-tar naphtha. The above classification is only fairly satisfactory, but it is impossible to adopt a scheme based on differences in chemical composition when in practice differences of physical properties are of greater importance. In the short summary of the properties of resins the special characteristics of a few typical members of each class will be given.

(*a*) **Oil Varnish Resins : Copals.**—These are essentially fossil, recent fossil, and recent resins. Some resins classed as copals are now a yearly crop and are used in oil varnishes. At present the bulk of the copal used for oil varnishes in this country is of fossil origin, obtained from Central Africa (Congo), Zanzibar (Animi), West Africa (Angola), Manila and the East Indies and New Zealand (Kauri). The supplies of fossil copals are limited and sooner or later the softer copals obtained from living trees will have to be utilized. It is stated that the supply of kauri copal will last for forty years

at the present rate of output (U.S. "Commerce Report," No. 281, 1915). The resin is fossil from *Dammara australis* (a species of New Zealand pine). The gum obtained from living trees is known as young kauri and is softer and almost colourless. Young trees, when tapped, yield the resin, and it is not uncommon to find deposits of resin in old trees. For fresh sources of copals it is probable that the belt of country extending from Madagascar to Sierra Leone and possibly the Gambia will be the most promising. The fossil East African copals (Zanzibar, Madagascar, Mozambique, Lindi) are highly prized. The Zanzibar animi copal, with its peculiar "goose skin" appearance, occurs in various sized pieces but not in large masses like kauri and other gums. It cannot be scratched by the finger nail: its melting point is 240°–250° C., and its "running" temperature is much higher. Böttler found the melting point of some samples as high as 340°–360° C. (chapter on "Varnish Making"). The East African fossil gums are derived from a species of trachylobium occurring in Madagascar, in German and Portuguese East Africa, and probably in British East Africa. The West African copals (Red Angola and Congo), are probably derived from *Copaifera mopane,* which occurs in the great forests along the Zambesi valley. In Southern Nigeria, the Gold Coast, and Ashanti, *Daniella oblonga* is the source, and in Sierra Leone and French Guinea *Copaifera guibourtiana.* Unfortunately the forests have been much depleted by wasteful tapping. All the copal obtained from British West Africa comes from living trees and is not a fossil resin. In Sierra Leone the trees are tapped on a definite system which consists in cutting out portions of the bark about 2 to 3 inches square at intervals of about 9 inches on the surface of the stem and larger branches of the tree. The process resembles tapping for rubber or turpentine resin, but it is more difficult, because rubber latex is secreted in lactiferous cells lying near the surface, while the resins are secreted either in isolated vesicles in the bark or in resin ducts lying in the bark or sap wood; moreover, the trees do not show such a "wound response"

as in the case of the Para rubber tree, which gives a large increase of latex on second tapping. Restrictions are now placed on unsystematic tapping and the Colonial Governments are endeavouring to increase the production of copal by planting trees and improving the yield of the resin (T. H. Henry, "Some Colonial and Indian Resins," *Proc. Paint and Varnish Soc.*, 1913).

The Manila copals are derived from *Agathis loranthifolia* and appear on the market as Manila, Borneo, Macassar, and Pontianak copals. The trees are tapped by a method resembling the "box" system used for turpentine resin in the United States. In Manila long strips of bark are cut from the trees and the exuded resin is collected as soon as the latter has dried hard: the same method is used in the collection of dammar gum. The softer varieties of Manila copals are soluble in methylated spirit, while the hard varieties are used by some varnish makers, although they have not the popularity of the African copals and the New Zealand kauri. The Brazilian copals are not in great demand because of their softness.

The copal resins are graded according to hardness, colour, fusibility, ash content, acidity, and loss of weight on "running." The following scale of hardness has been suggested by Böttler who takes, as standard, Zanzibar copal.

Zanzibar copal, Mozambique, Lindi, Red Angola, Pebble, Sierra Leone, Yellow Benguela, White Benguela, Cameroon, Congo, Manila, White Angola, Kauri, Sierra Leone (new), Hymenea [S. America, Brazil, Demerara, from the locust tree]. These copals are in order of descending hardness.

In lustre and colour the copals are vitreous, transparent, dull, colourless to yellow, reddish yellow and black. A vitreous gum is preferred to a dull cloudy resin. In fusibility the hardest copals have the highest melting points. Zanzibar melts at 240°–250° C.; West African copals melt at 120°–180° C.; Sierra Leone, 125°-137° C.; Manila and Kauri, 115°–140° C.; Hymenea copal (fossil), 180°–200° C., but the softer varieties melt below 115° C. The fusibility depends

essentially on the age, the new varieties fusing at lower temperatures. In view of the complexity of composition no fixed temperature can be assigned to any variety. It must be pointed out that the resins first soften and then slowly liquefy and the running temperature is the point when suitable fluidity is attained which may or may not coincide with the melting point. For each gum there is a temperature below which it cannot be incorporated with linseed oil.

A similar case might be quoted in the melting of sulphur as regards the necessary fluidity. Generally the softer copals are easier to work in every sense of the term.

Acidity.—This is a number of considerable importance in the evaluation of copals. If a resin mixing is considered from the standpoint of a colloid the acidity factor must not be neglected. The acidity of a "run" gum is not the same as that of the native copal: usually it is reduced to half its original value. A high percentage of esters is indicated by high saponification value (see Table of Constants of Resins).

Constants of Resins.

	Specific gravity.	Melting point.		Acid value.	Saponification value.	Iodine value.
		Softens.	Fuses.			
Kauri, brown ..	1·053	90° C.	185° C.	93·0	—	119·5
,, fused ..	—	—	—	63·0	—	—
Manila, hard ..	1·065	80°	190° C.	72·8	227·1	90·6
,, soft ..	1·060	45°	120° C.	145·2	—	—
Dammar, Batavian	1·031	—	100° C.	(20–35)	47·0	63·6
Mastic	1·057	—	95° C.	50–70	79·1	64·4
Rosin	1·07	80° C.	100° C.	145–185	168·2	112·0
Copal, Zanzibar ..	1·058	—	360° C.	60–65	92·4	—
,, ,, fused	—	—	—	61·0	37·0	126·8
,, Sierra Leone (A)	1·0645	—	195° C.	—	84·6	—
,, ,, ,, (B)	1·066	—	200° C.	—	130·0	—
,, Red Angola ..	1·066	90°	145°–315° C.	129·0	132·0	63·0
,, Benguela ..	1·058	65°	140°–160°	134·0	146·0	60·5
,, Brazil ..	1·053	50°	100°	112·0	151·0	59·0
,, amber ..	1·080	—	280°–315°	15–35	87·0	62·1
,, sandarac ..	1·073	—	145°	95–160	174·0	160·0
,, shellac ..	1·113–1·214	—	—	63·0	203·0	8·24
,, turpentine (oleo resin)	0·856	—	130° C.	69·8	—	143·6

Action of Solvents on Resins.

Percentages of *insoluble* matter (Coffignier, "Manuel du fabricant de vernis, gommes, résines").

	Turpentine.	Alcohol.	Ether.	Benzol.	Petrol ether.
Zanzibar copal ..	100·0	85·9	75·0	88·0	Insol.
Benguela ,, ..	69·0	16·5	43·7	65·6	,, or almost insol.
Kauri ,, ..	77·5	7·0	62·0	67·0	,, ,, ,,
Red Angola ,, ..	77·0	71·0	88·0	70·0	,, ,, ,,
Congo ,, ..	68·0	25·0	48·0	60·0	,, ,, ,,
Pontianak ,, ..	66·0	sol.	46·0	63·0	,, ,, ,,
Sierra Leone ,, ..	71·0	62·0	48·0	57·0	,, ,, ,,
Manila, hard ,, ..	73·0	56·0	58·5	64·0	,, ,, ,,
,, soft ,, ..	64·0	sol.	28·7	58·0	,, ,, ,,
Brazilian ,, ..	48·0	38·0	30·0	40·5	,, ,, ,,
Dammar	sol.	29·0	4·0	sol.	Soluble.
Mastic	sol.	36·0	sol.	,,	Almost insoluble.
Sandarac	74·0	sol.	,,	67·0	Partly ,,
Shellac	insol.	sol.	insol.	almost insoluble	,, ,,
Rosin	sol.	,,	sol.	sol.	Partially soluble.
Elemi	,,	,,	,,	,,	Soluble.
Benzoin	part sol.	,,	part sol.	insol.	Part soluble.
Madagascar copal ..	60·0	74·0	65·0	78·0	Insoluble.
,, ,, fused	4·0	92·0	52·0	1·5	Partly soluble.
,, after naphthalene treatment	52·0	75·0	20·0	40·0	,, ,,

The ash content ought to be very low. A West African copal may contain 0–2·2 per cent., depending on the grading.

The loss in weight on "running" is given as more or less 25 per cent., but it cannot be relied on, because it is entirely dependent on the process employed. Some state that the desired conditions of incorporation with linseed oil can be effected without loss in weight (H. Terrisse and Indestructible Paint Co., *J. S. C. I.*, 1904, *23*, 582, and 1908, *27*, 457). The process is essentially a depolymerization, but the complexity of the gums must admit of partial decomposition of component acids, with the liberation of liquid hydrocarbons (copal oil) and the formation of acidic anhydrides and lactones.

Spirit Varnish Resins

The second class of resins includes dammar, mastic, and sandarac.

Dammar.—This resin is a typical exudation from *Dammar orientalis*, indigenous to Dutch East Indies and British Malaya. It comes into the market in the form of nodules, clear and pale in colour. Dammar is decidedly softer than the majority of the copals, but harder than rosin. It dries with a "tack," and as a spirit varnish it gives a friable coat which can be easily rubbed up as a powder. Black dammar is an Indian resin.

Mastic.—This resin is the most important European form known with the exception of colophonium. It occurs in the Mediterranean littoral, being obtained from *Pistachia lentiscus*. Much comes from Greece either as cake, large or small mastic. The *Pistachia* has a marked wound response, so that under good conditions a tree may yield 8–10 lbs. per annum. Mastic is used as picture varnish, and with boiled linseed oil forms "megilp," the well-known artists' medium.

Sandarac is a North African resin exudation from the *Alerce* tree, indigenous to North Africa. It is a comparatively hard resin and is used to impart this property to mixtures with other resins. It is an ingredient of negative varnishes, label varnishes, and bookbinders' varnishes. It is soluble in methylated spirit and in ether, but only partially soluble in turpentine, petroleum, and benzol.

Lac.—The most important spirit soluble resin is Lac, considered by most investigators to be the secretion of the lac insect (*Tachardia lacca*) which is found on a number of species of Indian trees, *e.g.* acacia, ficus, mimosa, etc. The larvæ of the insect puncture the bark and feed on the sap. The lac excreted gradually imbeds the insects, but respiration is maintained through passages which contain wax penetrating the resin. The females, after fertilization, secrete a red fluid, the lac dye, and die on the appearance of new larvæ. The insects do not move from that part of the tree on which they first swarm. The production of the lac continues until the tree dies. Recently artificial propagation of the insect has been resorted to, so as to be independent of casual distribution by birds or other insects. The province of Bengal is the most important source of lac,

but it is produced in Ceylon, Burmah, Siam, China, and the Malay Archipelago.

Lac has several forms in which it comes on to the market.

(1) Stick lac, (2) Seed lac, (3) Shellac, (4) Button lac, (5) Garnet lac.

(1) *Stick lac* is the crude product direct from the trees in the form of short pieces of twigs encrusted with lac.

(2) *Seed lac* is obtained by breaking the twigs and removing the wood followed by treatment of the broken lac with warm water which extracts the lac dye: this may be recovered from the solution by evaporation.

(3) *Shellac* is obtained from seed lac by fusion and straining the melted lac through cloth bags. The molten lac is spread over the surface of a metal or porcelain cylinder and detached with a knife when solid. Orange shellac is sold in the form of flakes and is the best quality.

(4) *Button lac* is shellac in large round flat pieces of a dark ruby colour.

(5) *Garnet lac* is a variety which has been deprived to a very large extent of "wax" and appears in the form of thick flat pieces.

The native methods of treatment are very crude and have been replaced by modern methods in several of the Indian factories. The uses of shellac are given in the chapter on spirit varnishes.

Stick lac contains 66 per cent. resin, 6 per cent. wax, 6 per cent. gluten, and 11 per cent. colouring matter. Lac is soluble in methylated spirit, giving a turbid solution due to insoluble wax. It is insoluble in petroleum spirit but partially soluble in ether, chloroform, and turpentine (*vide* Constants and Solubilities, p. 87).

Shellac always contains rosin; which is added in the manufacture to lower the fusion temperature of the lac; orange shellac usually contains 1–2 per cent., garnet and button lac from 10–20 per cent. Increasing amounts of rosin render the shellac coating friable and powdery. Comparison of the iodine values of shellac and rosin (see Constants) indicates a method for estimation of the added rosin.

Shellac, when applied to a warm metal surface, gives a hard lustrous coat which, indoors, is a very valuable protective coating. In a damp atmosphere it disintegrates and is useless for outdoor work. The film becomes rough and powdery and does not regain its form on drying. As a hard priming undercoating on wood under varnish it is satisfactory, especially if the woodwork contains knots, but it is stated to be inadvisable to prime knots with shellac previous to the application of paint (Gardner, "Paint Researches," 1917, p. 347). Its electric insulating properties are high. Shellac is soluble in alkalies, alkaline carbonates, and borax. This property is utilized for the preparation of shellac water varnishes and to produce a bleached shellac soluble or partially soluble in alcohol.

Weak alkaline solvents remove the colouring matter from the crude shellac. It is remelted and pulled out in warm water. To bleach the shellac it may be dissolved in alkalies and chlorine passed in. The precipitated lac is collected, melted under water, and, when soft, is pulled so as to give it a fibrous satinlike appearance. The bleached shellac has to be kept under water to prevent it losing its solubility in spirit, and even under these conditions it gradually deteriorates. The spirit soluble form is a component of the so-called colourless lacquers. Bleached shellac is rarely completely soluble in methylated spirit. A lac water varnish is a water solution of shellac or bleached shellac in borax; it makes a good waterproof paper varnish.

Turpentine, Rosin, and Rosin Oil.—There is frequent misunderstanding in the nomenclature of the products of the resinous exudations of the varieties of Pinus. Turpentine was the name given originally to the exudations which are semifluid and in their raw state appear in the market under such names as Venice Turpentine or Strasburg Turpentine. On distillation of the oleoresin, turpentine oil ("spirits of turpentine") is obtained. The non-volatile product is rosin (colophony, colophonium), which on dry distillation furnishes a volatile rosin oil and a residue of rosin pitch. The turpentine used in Europe is practically all obtained

from the United States, France, and Russia, with smaller quantities from Spain, Portugal, Algeria, and Greece. Russia is the only country which can increase its output largely, although Russian Turps is less popular than the American variety for reasons stated below. Central America is as yet an undeveloped area (Mexico and British Honduras). Within the British Empire, Honduras and India possess pines which yield a flowing oleoresin, but in India the industry has been developed only for the home market. The yield of crude resin (gum thus) varies with the species of Pinus. In America incisions are made in the trees in winter and in March the sap begins to flow. The resin is collected in suitable boxes attached to the trees. After four years' tapping the trees are felled and used for lumber. The system has to be as carefully controlled as in the case of rubber; if the tapping is too drastic the tree dies or the yield falls off, moreover, replanting of the trees must be systematically maintained (Tschirch, "Die Harze u. die Harzbehalter"). The most important American varieties of turpentine-yielding pines are: *Pinus australis* (Georgia pine) and *Pinus tæda* (the loblolly pine). It must be pointed out that resin is found in all varieties of pine, but only a few give a flow of sap after incision of the bark. Five hundred gallons of crude turpentine oleo resin yield 125 gallons of turpentine and the residue is rosin. The Central American pine is *Pinus Cubensis*. The French variety is *Pinus maritima* and in that country the turpentine industry is more carefully regulated than in America. In the neighbourhood of Bordeaux, in the Departments of Les Landes and Gironde, the cultivation in the shifting sands of the Gascon dunes has been developed since the end of the eighteenth century.*

Russian turpentine is obtained from *Pinus sylvestris* by methods which are wasteful and primitive in comparison with those adopted in America and France.

In Russia and Sweden pine stumps are placed in trenches dug in the ground having iron-sheeted bottoms under which

* For a comprehensive account of the French turpentine industry cf. Joly, *Proc. Oil and Colour Chemists' Assoc.*, 1920, *15*, 149.

fires are started to distil the turps from the stumps. In India there are large tracts of pine forest in the Punjab, the United Provinces of Agra and Oudh. The production of turpentine in 1911 in the United Provinces amounted to 27,000 gallons, all consumed in the country. Unfortunately it is slower drying than the American variety, containing less volatile terpenes (F. M. Perkin, *Paint and Varnish Soc.*, 1913).

It is evident that unless the cultivation of the tree and the extraction of the resin is carried out in an economical manner shortage will occur and prices will rise. There are many resin-bearing species of *Pinus, e.g. Pinus palustris* (long-leaved pine) and the Douglas fir (British Columbia), which do not give any yield on tapping, but the resin may be extracted by destructive distillation or by steam distillation. Another source is the by-product in the wood pulp industry, especially in Scandinavia. Wood turpentine is marked by a peculiar wood essence-like smell and apart from this possesses the main properties of turpentine, but is always coloured. On an average 1½ gallons of turpentine are obtained from 100 cubic feet of wood.

The oleoresins from the genus *Pinus* may be used as such or distilled to give turpentine and rosin (colophonium).

Canada balsam is the oleoresin from *Abies* (*Pinus*) *Canadensis;* Strasburg turpentine from *Abies pectinata* (silver fir) ; Venice turpentine from *Pinus larix* (larch).

According to Tschirch (*loc. cit.*), Canada balsam (a typical oleoresin) contains : canadinic acid, 13 per cent. ; canadolinic acids, 48–50 per cent. ; canadoresene, 7 per cent. ; essential oil (turpentine), 23–24 per cent.

The flowing oleoresin from the pines of France and America, etc., is exuded as a transparent liquid which becomes viscid and turbid in contact with air. Generally it has the consistency of honey, and is coloured and turbid. The oleoresin from *Pinus maritima* contains 18 per cent. turpentine, 70 per cent. rosin, 10 per cent. water, and 2 per cent. impurities. The yield of oleoresin is variable with the species; Tschirch gives 20 per cent. (French and American), Schkateloff gives 13–20 per cent. for Russian pines.

To obtain turpentine from the oleoresin it is distilled in a current of steam under conditions which vary locally (*vide* F. M. Perkin, *loc. cit.*). Wood turpentine oil is obtained by the destructive distillation of tree stumps and consequently many additional products are obtained, *e.g.* wood alcohol, acetic acid, creosote heavy oils, charcoal, but no rosin. In British Columbia the pine wood is distilled in brick retorts electrically heated and the temperature controlled so that it does not rise above 205° C. The products are turpentine, rosin, tar oil, tar, and charcoal [Livache and McIntosh, "Manufacture of Varnishes," Vol. 3, 2nd edition].

Turpentine is a mixture of terpene hydrocarbons and its composition varies with the source. In America turpentine dextro-pinene, $C_{10}H_{16}$, occurs; French turpentine contains terebenthene (lævo-rotatory), $C_{10}H_{16}$; Russian turpentine contains sylvestrene, $C_{10}H_{16}$, which is dextro-rotatory.

Wallach and his pupils have made a close study of the natural terpenes, and of late years a number of terpene hydrocarbons have been synthesized by Perkin, so that the structural formulæ are fairly well established. In practice it is rarely necessary to isolate any of the characteristic derivatives of the terpenes and the standards given below are adequate :—

	S.G. 15° C.	Flash point [Abel].	% fraction boiling below 160° C.	% fraction boiling below 170° C.
American turpentine	0·862–0·87	86–88° F.	72–78%	95–97%
French turpentine ..	0·864	,,	,,	,,
Russian turpentine	0·861	93° F.	8%	65% below 170° C. 80% ,, 175° C.
American wood turpentine	0·859	,,	—	below 170°C.—35% ,, 175°C.—80% above 180°C.—20%

It must be remembered that pinene undergoes decomposition above 250° C. and gives resinous products, so that care has to be taken not to exceed that temperature during the dry distillation of wood.

The terpenes are ring compounds containing unsaturated linkages and asymmetric carbon atoms, so that the variety of their derivatives is great and their activity is very marked.

Constants of Terpenes.

	B.P.	S.G.	$[\alpha]_D$	Hydrochloride.	Nitrosochloride.
Pinene ..	155–156° C.	0·857/20°	$\left\{\begin{matrix}-43{\cdot}4\\+32{\cdot}0\end{matrix}\right\}$	$C_{10}H_{16}HCl$, m.p. 125° C.	$C_{10}H_{16}NOCl$, m.p. 115° C.
Sylvestrene..	177°	0·851	+66·3	$C_{10}H_{16}{}^2HCl$: $C_{10}H_{16}Br_4$ m.p. 135° C.	$C_{10}H_{16}NOCl$, m.p. 106°–7° C.
Limonene ..	176°	0·846	+106·8	$C_{10}H_{16}Br_4$ m.p. 104° C.	—
Phellandrene	170°–2° C.	—	—	nitrite, m.p. 103°–4° C.	—

The properties of the last two are mentioned because of their connection with the products of the " running " of copals.

The important properties of turpentine from a practical standpoint are: (1) solvent properties for oils and resins; (2) drying properties and action as a catalytic oxygen carrier. Turpentine is a good solvent for sweated copals, rosin oils, for metallic salts of drying oils and metallic resinates, *e.g.* manganese linoleate and manganese resinate.

American and French turpentine evaporate easily at the ordinary temperature, leaving a slight greasy residue. Russian turpentine leaves a much larger greasy residue, similarly wood turpentine, so that these two varieties are not considered to dry hard. Turpentine absorbs oxygen readily from the air forming a peroxide: when pinene is exposed to the air and light sobrerol, $C_{10}H_{16}O_2$, is formed (Armstrong). No doubt during the evaporation of turpentine greasy oxidation products are formed which may bind any dissolved resin; generally speaking any catalytic oxidizing powers may be considered small compared with those of drying oils (cf. Turpentine Substitutes).

Turpentine Substitutes

With the steadily rising price of turpentine and the prospect of world shortage, unless the cultivation of the pine forests is methodically organized, it is only natural that substitutes for turpentine will be welcomed. The requirements are solvent power equal to that of turpentine and air-drying power as rapid, leaving little or no volatile residue. The flash point must be above 73° F. to conform with transport requirements. The smell must be pleasant and resemble that of turpentine as much as possible. The

basis of turpentine substitutes nowadays is a petroleum blended with turpentine in varying amounts. If a petroleum can fulfil the above requirements the use of turpentine is unnecessary. A short reference must be made to several factors which are of considerable importance.

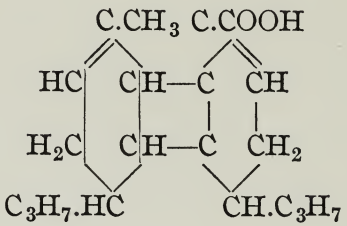
The petroleums are generally not such good solvents for gum-oil mixings or for metallic driers, nor have they the same viscosity and flow as turpentine. From the experiences of the 1906 Test Fence of the North Dakota Experimental Station (Ladd and Washburn, *Bulletin*, 1915, *1*, 73), the substitution of petroleum for turpentine does not give the same results as where turpentine in moderate amount is used. It is probable that the slight greasy residue of oxidized turpentine facilitates the retention of the resin in solution (raw resins are more soluble in oxidized turpentine than in turpentine). Friend (*loc. cit.*) finds that for paints on iron turpentine and petroleum media are equal. The petroleums offered are so varied in composition that for comparison only volatility tests can be carried out; generally the presence of aromatic hydrocarbons tends to improve their solvent power. There would appear to be no definite evidence that turpentine assists the catalytic oxidation of the gum-oil drier mixing. It was supposed that any kind of petroleum would cause "bloom" in varnishes, but this is incorrect. For the estimation of petroleum in turpentine cf. Lunge and Keane, "Technical Methods of Chemical Analysis," Part 1, Vol. 3, also *Chem. Zeit.* 1918, *42*, 349–351.

Colophony (Rosin).—In the distillation of turpentine oleoresin in a current of steam, after the turpentine has come over, rosin is left in the stills. The purification of French rosin includes (1) drying to expel water, which would otherwise leave the rosin opaque, (2) filtration of the fused rosin, (3) moulding whereby the filtered molten rosin is run into suitable moulds, (4) bleaching by exposure of the moulded rosin to the sun's rays (Livache and McIntosh, *loc. cit.*). Rosins are graded according to paleness; "window glass" rosin is clear and of a pale amber colour; common rosin is clear but darker; black rosin is opaque and very dark.

Rosin contains abietic acid $C_{20}H_{40}O_2$, with its isomers pinic acid and sylvic acid (Paul, *Seif, fabr.*, 1916, *36*, 545; *Z. angew. Chemie*, 1915, *28*, 415).

American rosin contains 90 per cent. pinic acid (m.p. 70° C.) and sylvic acid (m.p. 122° C.). Pinic acid has been isolated in three varieties, α, β, γ, with different melting points. γ-pinic, sylvic, and γ-abietic acids are soluble in petroleum ether while α and β-pinic acids are insoluble. Abietic acid from Spanish rosin is identical with the acid obtained from American colophony (Blanes, *J. Chem. Soc.*, 1915, *108*, 1493).

The formula $C_{20}H_{30}O_2$ proposed by Fahrion (*Chem.*



Revue, 1913) was put forward by Bischoff and Nastvogel in 1880. As in the case of the copal resins much research work is yet needed in elucidating the composition and formula of abietic acid and its isomers.

Colophony (colophonium) contains resenes which in the case of copal resenes may be regarded as oxypolyterpenes formed from terpenes by simultaneous oxidation and polymerization. In spite of uncertainty of its formula sufficient is known to connect its probable structural formula with its most important practical uses. It is an acid resin, soluble in most organic solvents, giving a lustrous film of low durability and hardness; it is an unsaturated body, able to absorb oxygen and reacting with metals, *e.g.* lead, manganese, and cobalt, in the same way as the drying oil acids, *i.e.* as an oxidizing catalyst. In this connection the resinates of lead and manganese and cobalt are largely used; they are soluble in turpentine and to a slightly less degree in the turpentine substitutes. The tackiness of rosin films can be corrected by

addition of lime or zinc oxide whereby the film is hardened, but it is prone to hydrolysis by water.

Rosin esters can be obtained by condensation of alcohols under various conditions, *e.g.* glycerol, resorcin, naphthol. The ester gums are pale in colour, unacted on by water and can be easily incorporated with oil, thereby improving the water-resisting properties of the film. The properties of ester gums have been investigated by Ellis and Rabinovitz (*J. Ind. Eng. Chem.*, 1916, *8*, 406), with special consideration for preventing "livering" of the vehicle in the presence of pigments. This paper is of interest in giving a summary of the published work to date. Rosicki (*Farb. Zeit.*, 1913, 1194) considers that the reduction in the acidity of the resins is a necessary condition, whereas Muehle (*ibid.*, 1913, 119, 1944; 2058 and 2178) is of opinion that the coagulation ("livering") is due to association of copal particles rather than to the formation of insoluble salts, because he was unable to produce varnishes from Congo and Manila copals which would stand the addition of pigments either after esterification or reduction in the acid value. Meguele (*ibid.*, 1913, 2230) considers there is truth in both views and the verdict of practical experience will support him.

Rosin Oil.—When rosin is heated in a closed vessel it undergoes destructive distillation; the heating may be by direct fire with or without introduction of superheated steam. The conditions of distillation modify the proportions of the products. The products consist of :—

	Dry distillation.	Fire heat and superheated steam.
Gas ..	.. 5·4 %	—
Acid water	.. 2·5 % (containing 10 % acetic acid)	—
Rosin spirit	.. 3·1	15·0
Rosin oil ..	.. 85·1	64 %
Pitch ..	.. 3·9	—

The rapidity of the distillation has an effect on the proportion of the products. Hard rosin oil is produced when the distillation is conducted rapidly and during the first stages of distillation, whilst soft rosin oil is produced when the process is conducted slowly and during the middle period of the distillation. The gas is of value for illuminating

purposes, and from the acid water calcium acetate is prepared. The properties of rosin pitch will be referred to under "Pitches." In France the addition of lime to the rosin causes an alteration in the composition of the products. For the paint and varnish industry the demand for rosin oil is insignificant compared with its utilization as a lubricant. The better qualities of rosin oil have no drying properties and the crude varieties are feeble in that respect.

Rosin spirit is said to contain a fluid hydrocarbon C_7H_{12}, b.p. 103–4° C., and hexylene and amylene occur in light rosin spirit. Rosin spirit may be present in turps substitutes, but if the latter contains rosin oil it will dry greasy and will not distil over below 250° C.

Chinese and Japanese Lacquer.—There are two genera of plants belonging to the natural order *Anacardiaceæ* containing species which, on being tapped, yield a sap largely used in the East as natural varnish or lacquer; these are Rhus, which yields Japanese lacquer, and Melanorrhea which produces the black varnish of Burma. The Japan lacquer is characterized by:—(1) hardness, which increases with age, (2) lustre, which is retained under varying atmospheric influences, and (3) resistance to the usual agencies which attack varnishes (*Bulletin of the Imperial Institute*, 1910, *8*, 32). The tree which yields Japanese and Chinese lacquer is *Rhus vernicifera*. It is found in woods at an elevation of 4000 feet and cultivated along the margins of fields or valley bottoms. The tapping of the tree for sap resembles that of the *Pinus* for turpentine oleoresin. Large quantities of the varnish pass annually through the Port of Hankow. In 1908, 2,479,702 lbs. were exported, the bulk of which went to Japan. The raw varnish, which is frequently adulterated with Tung oil, is known in Japan as Ki-urushi. When first collected the sap is of grey-brown colour of viscid consistency, turning black on exposure to the air and becoming coated with a thick tough skin. The only method of thinning the lacquer known to the Japanese is by adding camphor. The peculiarity of the substance is that it hardens only in a moist atmosphere and remains

in a tacky condition if exposed to sunlight and heat. Its application in China is performed only in wet weather or in a damp atmosphere. Oxygen to 5·75 per cent. by weight is absorbed in drying at the ordinary temperature: whether the catalyst is an ordinary ferment (laccase) or the activity is due to the presence of manganese with a proteid-like substance is undecided. For a concise description of the manufacture of Chinese and Japanese lacquer reference may be made to *Bulletin of the Imperial Institute* (*loc. cit.*).

The Burmese black varnish or lacquer (thitsi) is an oleoresin obtained from the black varnish tree *Melanorrhea usitata*. The trees are tapped, and in general properties the lacquer is similar to that obtained from Rhus, although slower in drying. ("Drugs, Oils, and Paints," 1917, *32*, 413.)

The application of the lacquer is said to be dangerous to western workers owing to the peculiar poisonous properties of the resin.* Majima and Tahara (*Ber.*, 1915, *48*, 1593) have synthesized hydrourushiol dimethyl ether obtained from "urushiol," the chief constituent of Japan lac. From their investigations Japan lac is an aromatic derivative with a long side chain, since hydrourushiol dimethyl ester has been shown to have the formula,

$$(CH_3O)_2C_6H_3(CH_2)_{14}CH_3.$$

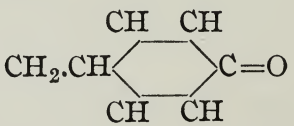
For durability Japan lacquer far surpasses any other resin known.

Synthetic Resins.—When phenols and formaldehyde (formalin) are heated in the presence of condensing agents substances are obtained which in appearance and properties resemble natural resins, especially Indian lac. The condensing agent may be an acid, an alkali, or ammonia. The investigation of these substances has been developed by Baekeland and his collaborators. The chief representative of the class of synthetic resins is Bakelite, which is manufactured in a number of forms, each with important properties. An account of Bakelite and its applications is given by H. Lebach (*J. S. C. I.*, 1913, *32*, 559). The

* Recent experience has shown, however, that the poisonous properties have been much exaggerated.

so-called Bakelite varnishes are solutions of Bakelite "A" in methylated spirit. The varnishes when stoved give hard insoluble and infusible coatings of high chemical and mechanical resistance. Stoved Bakelite lacquer films resist the action of methylated spirit, ammonia, and salt water, moreover they are acid proof. Bakelite is used for the impregnation of coils, armatures for magnetos, arc lamps, transformers, etc., because of its great dielectric strength. If fluid Bakelite "A" (Resole) is heated for several hours at a temperature of 140°–170° C., and at a pressure of 10 atmospheres, it is transformed into transparent, insoluble, and infusible Resite. Generally a filling material is used, which is impregnated with the fused resole forming a plastic mixture, which completely fills the mould in the press. At a temperature of 100°–200° C. the resole is changed to Bakelite "C" (Resite). Resite is non-hygroscopic and is the most resistant of all plastics; it can be heated to 300° C. without decomposition and at higher temperatures it chars but does not ignite. It is suitable for pen and pencil holders, umbrella handles, cigar holders, etc.

The Resites are considered by Wohl (*Ber.*, 1913, *45*, 2046) to be polymerization products of methylene derivatives of the tautomeric phenol



Furfuraldehyde can replace formaldehyde in these resins (*J. S. C. I.*, 1920, 577A). In oil varnishes (Albert and Behrend, Eng. Pat., 15875/1914, and Ger. Pat.,281939/1913) they have had only a limited success. A new class of artificial resins (cumarone resins) has attracted attention lately. These resins are polymerization products of cumene and indene (obtained from crude benzol (b.p. 160°–180° C.) by the action of sulphuric acid (Böttler, *Kunstoffe*, 1915, *5*, 277, and Krumbhaar, *Farb. Zeit.*, 1916, *21*, 1086). The cumarone varnishes are said to be tacky, and although they can be hardened by the addition of paraindene, yet their durability is poor.

Unaccountable thickening ensues when cumarone varnishes are mixed with certain pigments.

The acrylic acid esters prepared from glycerine, lactic acid, etc., when exposed to sunlight or ultraviolet light polymerize to varnish-like elastic masses. They are soluble in solvents for oils and are stated to dry rapidly and not to be readily affected by exposure or by chemical agents (*J. S. C. I.*, 1916, *35*, 698).

Accroides Resin. — Xanthorrhea, or grass tree (*Juncaceæ*), is confined to Australia and Tasmania. It is a plant with a short thick woody stem, terminated by a tuft of long leaves about 3 feet with cutting edges. The three most important species are *X. hastilis* and *arborea* (red gum accroides), and *X. australis* (yellow gum accroides). From the trunk of the trees on incision flows a resinous substance giving a layer 2–4 cm. thick in the case of *X. australis*. Sometimes fragments detach themselves spontaneously and collect at the foot of the tree where they are found buried and semifossilized.

Red gum accroides approximates Dragon's Blood in colour, with a shade approaching brown, possessing an orange streak. In lustre, however, it is superior. The yellow variety differs only in colour and in structure from the red variety (Livache and McIntosh (*loc. cit.*), Vol. 3, and Seeligman and Zieke, "Handbuch der Lack u. Firnis Industrie" (1914)). Both varieties are soluble in alcohol and alkalies but insoluble in petroleum ether, in that respect resembling shellac. Xanthorrhea resins seem to belong to the same class chemically as Peru balsam, storax, and benzoin. During the War it was suggested that they might be transformed into picric acid by comparatively simple nitration.

Pitches

Pitches.—The mineral pitches comprise bitumen or asphaltum (French, Asphalte; Spanish, Asfalto; German, Erdpech). The term "bitumen" is considered by Langton (*Proc. Oil and Col. Chem. Assoc.*, 1919) to be generic, defining a class of substances soluble in carbon disulphide

and other neutral liquids and consisting of compounds of carbon and hydrogen associated frequently with compounds of oxygen, sulphur, and nitrogen. Asphalt would be regarded as mineral matter containing bitumen in intimate association.

The artificial pitches or residual pitches (Richardson, *J. Ind. Eng. Chem.*, 1916, , 4) are essentially the products of the distillation or destructive distillation of carbonaceous material in the form of coal (coal-tar pitch), petroleum (mineral oil pitch), resinous woods (Stockholm pitch, rosin pitch), vegetable and marine oils (stearine pitch), wool fat (wool grease pitch), and bones (bone pitch).

The above list shows their great variety with endless complexity of chemical composition, yet marked by characteristic differences as to hardness, blackness, fusibility, and brittleness.

In order of magnitude of production coal-tar pitch is the most important.

Coal-tar Pitch is the residue remaining in the stills after the first distillation of coal-tar and amounts to two-thirds of the weight of the treated tar or 4 per cent. of the weight of the coal carbonized. The lower gravity tars, produced at low carbonization temperatures, are rich in open chain paraffinoid bodies and give a lower yield of pitch than the high gravity tars containing aromatic hydrocarbons with free carbon. The softness and hardness of tar pitch depend on the conditions of distillation: a harder pitch being produced by heating the tar strongly to obtain the maximum yield of anthracene distillate and the residual hard pitch is graded by addition of creosote or anthracene oil. Stewart (*Trans. London and Southern District Junior Gas Association*, 1911–12, 43) states that at high temperatures and with light charges a yield of 78 per cent. pitch is obtained; continual distillation from vertical retorts gives 47 per cent, whereas moderate heat and fairly heavy charges give 56 per cent. pitch of finer quality and a lower content of free carbon. The specific gravity varies from 1·2 to 1·3. Soft coal-tar pitch softens at 37° C. and melts

about 60° C. Moderate hard pitch softens at 60° C. and melts at 80° C.: the hard variety softens at 80° C. and melts at about 175° C. The melting point is taken as the point at which the pitch becomes soft enough to flow. Little is known of the constituents except that they belong to the aromatic series (Marcusson, *Z. angew. Chem.*, 1918, *31*, 113).

	Carbon.	Hydrogen.	Oxygen.	Sulphur.
Hard coal-tar pitch ..	75·3	8·4	16·0	—
Trinidad asphalt (Keyser) ..	78·8	11·4	—	10·0

For the varnish maker the use of coal-tar pitches is limited by partial solubility in petroleum although they are freely soluble in coal-tar spirit.

Petroleum Pitches.—A rival to the coal-tar pitches are the residues left in the refining of petroleum. From all the refineries in America, Galicia, and Rumania grades of pitch are obtained suitable as road-binding material, asphalt, and cements. In 1917 the United States produced 701,809 short tons of petroleum pitches. In England these pitches are unable to compete with the cheaper coal-tar varieties for ordinary classes of work. They resist the action of acids and alkalies and possess good lustre, tenacity, high electric resistance, and adhesive power to metal surfaces. Some oils yield a softer pitch soluble in turpentine or petroleum so that it can be used in Japans or cycle enamels.

Bitumen or Asphaltum.—Bitumens are preferred for varnish purposes because of their hardness, lustre, and durability, and they furnish excellent black enamels. Some of the commoner varieties are:—Grahamite (Oklahoma), Gilsonite (Utah), Bermudez (Venezuela), Manjak (Trinidad), in addition to bitumens from Cuba, Colombia, and Syria. Some asphalts, *e.g.* Trinidad and Bermudez, are refined before being marketed. The natural asphaltums are generally soluble in petroleum except Trinidad pitch (partially soluble) and ozokerite pitch. They are unacted on by dilute acids and alkalies. For varnish making they should possess brilliant lustre, a conchoidal fracture, and not lose shape in boiling water. They should be practically free from ash

and be soluble in turpentine, petroleum, and high boiling-point coal-tar naphtha. The specific gravity varies between 1·1 and 1·2. The pitches soften at 60° C. and melt between 100° and 140° C. A summary of the literature on the subject may be found in papers by Langton (*loc. cit.*) and Donath and Strasser (*Chem. Zeit.*, 1893, *17*, 1788). An analysis of a bitumen shows the presence of carbon, hydrogen, and sulphur in approximately the following amounts which vary with the source: carbon, 74 per cent.; hydrogen, 10 per cent; sulphur, 16 per cent.

Stearine Pitches.—Stearine pitches are the residues from the distillation of vegetable and mineral oils or fatty acids. They are of value for blending with bitumens, possessing high lustre, satisfactory hardness, elasticity and solubility in turpentine and in petroleum. The pitches from drying and semi-drying oils are usually less soluble in the above solvents. Cotton-seed oil pitch is made by distilling cotton-seed black grease, prepared from the mucilage obtained in refining crude cotton-seed oil.

When unrefined cotton-seed oil is distilled the pitch is obtained in the form of a highly elastic spongy mass: this elastic cotton-seed pitch can be vulcanized and in that form is largely used in electric cables, but the coating is apt to be brittle at low temperatures. The harder varieties are used in the manufacture of waterproof paper.

Stearine pitches give a lustrous coating which is brown in thin layers; this defect may be neutralized by incorporation with **Bone Pitch**, an intensely black pitch obtained by the distillation of bone oil (Dippel's oil), produced when bones are dry distilled. Bone oil yields about 23 per cent. of hard pitch. Alone, bone pitch is not very soluble in solvents, but it can be blended with more soluble varieties. All the stearine pitches require sweating before incorporation into black varnishes to give coatings of satisfactory dryness.

Wool grease pitch is softer than stearine pitch (Donath and Margosches, *Chem. Rev.*, 1914, 1904), and is used as a lubricant rather than as a varnish pitch.

Stearine pitches can also be obtained from whale oil

fatty acids. It is probable that the constituents of stearine pitches are decomposition products of fatty acids and esters consisting of paraffinoid hydrocarbons, ketones, polymerization products, and complex esters which are more weather-resisting than the original oils. The softness, elasticity, and solubility depend on the source of the material and on the conditions of distillation.

Ozokerite.—Among the mineral pitches Galician ozokerite gives on distillation a hard waxy substance, breaking with a rough granular fracture. In colour it is dark amber, softening at 50° C. and melting between 85° C. and 100° C. Ozokerite and ceresin (the product obtained by refining ozokerite) are employed as "finishing wax" and in electric cables. Some qualities burnish well and take a high polish (Redwood, *J. Soc. Arts*, 1886, 34; Marcusson and Schulter, *J. S. C. I.*, 1905, *26*, 491).

Stockholm or Swedish pitch and Rosin pitch are typical products of the distillation of residues of wood tar and of rosin respectively.

Stockholm tar when distilled gives light oils, sp. gr. 0·84–0·88, and about 70 per cent. yield of pitch. The pitch is soft with a jet-like lustre, but of a brown colour in thin films. It is easily soluble in alkalies owing to the presence of phenolic bodies, *e.g.* guiacol and cresol, which endow it with marked preservative and antiseptic properties whereby it is largely used in the painting of ships. It enters into the composition of many impermeable cements and black varnishes. Prior to 1914 the annual yield from Russian sources was estimated at 55,300 tons.

Rosin pitch is the residue left on distillation of rosin (colophony) and amounts to about 15 per cent. of the rosin taken. It is a yellowish-brown substance with a rosin-like smell, possessing a sticky feel and crumbling easily on slight pressure. It dissolves in nearly all the solvents for colophony. Rosin pitch is rarely used alone in varnishes and is only occasionally blended with low-grade pitches.

In the examination of pitches the determination of the

softening and melting points is of importance as well as the specific gravity. In the stearine pitches the acidity and saponification values are useful, but in very hard fat pitches, obtained by pushing the distillation to its utmost limit, the values are low. A comparison of the acid and saponification values of stearine pitch and petroleum pitch is shown in the subjoined table :—

	Acid value.	Saponification value.
Stearine pitch ..	0·2–2·9 ; 2·4	2·2–8·3 ; 4·3
Petroleum pitch ..	0·1 ; 1·2 ; 0·3	1·3 ; 2·6 ; 1·7

The detection of wood-tar pitch is facilitated by the characteristic smell of creosote on heating and by complete solubility in alcohol. Coal-tar pitch contains a considerable amount of free carbon.

The methods of identification of the varieties of pitches are on the whole unsatisfactory. A scheme has been put forward by Mansbridge (*J. S. C. I.*, 1918, *37*, 184) which applies to single pitches, but not to mixtures. It relies on a division into saponifiable and unsaponifiable pitches and the behaviour of the members of the two divisions to the solvent action of white spirit. It looks promising in spite of several exceptions due to the variety of conditions in the production of these complex bodies. Lawton (*loc. cit.*) gives the results of the examination of a number of pitches, especially stearine pitches.

The natural asphaltums or bitumens containing sulphur and nitrogen can be separated into petrolenes, soluble in 88° C. petrol, and asphaltenes. Petrolenes are tough viscid substances possessing cementing properties, whereas the asphaltenes are dry and brittle, but soluble in carbon disulphide and in hot turpentine.

Petrol (88° C.) dissolves coal-tar or wood-tar pitches which would be used in varnish enamels, but the petrolenes are unsaponifiable by alkalies.

The discussion of the origin of the bitumen deposits is outside the scope of this book. As hydrocarbons, *e.g.* bitumen of the Dead Sea and Trinidad asphalt, they contain

carbon, hydrogen, oxygen, nitrogen, and sulphur, and yield on distillation gas, coke, burning oils, and gas oils, so that they are comparable with petroleum pitches produced artificially.

	Dead Sea asphalt.	Trinidad asphalt.
Carbon	77·8	78·8
Hydrogen	8·93	9·3
Nitrogen	—	1·4
Sulphur	—	10·0
Oxygen	11·54	—
	100·54	99·5

The pitch lakes of Trinidad and Bermudez represent important deposits of natural bitumen, but their origin, like that of the mineral oils, remains undecided.

Richardson (*J. Ind. Eng. Chem.*, 1916, *8*, 4) suggests that the petroleum pitches originate by surface action between natural gases and the sands with which they come in contact, and that asphalts are formed by the surface action of colloidal clays upon heavy petroleums. Peckham (*J. Frank. Inst.*, 146, (1) 45), from a study of the Californian bitumens, considers that the polymerization of petroleum and the conversion into asphalt is due largely to the presence of nitrogen and sulphur.

For full information on the examination of pitches reference may be made to the following works :—

Allen : " Commercial Organic Analysis " : " Thorpe's Dictionary of Applied Chemistry " (Pitches). Lunge and Keane : " Technical Methods of Chemical Analysis." Ingle : " A Manual of Oils, Resins, and Paints." Gardner and Schæffer : " The Analysis of Paints." Seeligman and Zieke : " Handbuch der Lack u. Firnis Industrie " (1914).

Part IV.—PIGMENTS, PAINTS, AND LINOLEUM

Section I.—PIGMENTS AND PAINTS

Pigments

The subject of pigments introduces a primary consideration of their uses in paints and enamels. Their employment as a means of obscuration of the undercoat for decorative treatment being obvious, the question of choice of paint or varnish to serve as a *protective* coat leads to a consideration of the general influence produced by a pigment in a paint. In applying a drying oil medium to a non-absorbent surface, the thickness of film applied is limited by mainly one factor, that of viscosity, and it is obvious that such is limited by considerations of practicability. The application of a thick film, however, can be realized by applying it in the form of a two-phase system of solid/liquid wherein the rigidity of the system is out of all proportion greater than its corresponding viscosity or resistance to shear. The net result of such is to furnish a means of applying a heavier or thicker coating than would otherwise be possible in the absence of the pigment. There are other influences at work in a paint in addition to these which will be considered under the heading of paint and enamels.

The several properties of the different pigments will be considered under their respective headings, but a review of the general properties of pigments used in paints will be necessary at this juncture. Pigments may have one or many of the following properties :—

(i) *Colour, Opacity, and Tinctorial power.* Although white is usually not considered as a colour, the fact that its function in paints is often to overcome or " kill " another colour makes it expedient to consider it as such. Tinctorial power is to be distinguished from the other property of pigment referred to as colour by the capacity for staining or imparting hue. The term " capacity " or " body " is more strictly accurate in referring to that property of a pigment which is distinguished by the capacity for obscuration of an underground or undercoat.* A sharp classification into staining and obscurative pigments is not possible, as certain pigments possess both properties, and the property of obscuration or opacity, although nearly absent in certain pigments, is only present to any degree in others under certain conditions. The main factor in obscuration is that of producing optical discontinuity in the film under consideration. This clearly resolves itself into the attainment of a layer or layers through which the light passing suffers different degrees of refraction. In other words, high opacity in a film is obtained by a combination of pigment and medium of refractive indices as far apart as possible. The medium may be oil, water, or air, so that it may happen that two pigments may have nearly the same opacity, examined dry or in water, but by virtue of a closer approximation of refractive index of linseed oil to that of one of the pigments, such may prove more or less transparent in an oil medium. The higher the refractive index of a pigment, therefore, the greater its opacity, since no medium exists which has a greater index of refraction than that of the most transparent of pigments. The ultimate size of the particles also has a great influence on the opacity of a pigment, the smaller the size of the pigment the higher the opacity, this latter property, however, diminishing as approximation in size to the wave-length of light is approached.

Tinctorial, or staining power is the relative degree to which unit weight of pigment will confer colour to another

* For a description of an ingenious laboratory apparatus for determining opacities of pigments, see Pfund, *J. Franklin Inst.*, 1919, *188*, 675–681.

to obtain the same degree of tone value. Thus two samples of Prussian blue will be compared for staining power by determining the relative amounts of white pigment necessary to obtain pale blues of similar "tone" or light reflecting value. The converse of this property of staining power, sometimes referred to as "killing power," represents the result of a similar determination on a white pigment, and the procedure is self-evident. The two properties of opacity and staining power do not necessarily bear any relationship towards each other, though usually a close relationship sometimes exists between opacity and "killing power" of white pigments. Thus Prussian blue represents a pigment of high staining power and very low opacity, Indian red possesses both great staining power and high opacity, whilst the chromes possess moderate staining power and high opacity. The high opacity of most black pigments is probably accounted for by their power of absorbing light to a great degree as well as by their high state of subdivision.

The colour of pigments often varies to a great degree according to their method of preparation. Whilst comparatively small variations are found in certain classes of pigments such as Prussian blue, great variations in hue are to be found among the earth colours and chrome pigments.

The measurement and registration of colours in numerical terms has been attempted by many investigators. One of the best-known instruments is that of J. W. Lovibond, known as the "Tintometer." In this instrument a flattened heap of the pigment under examination is viewed simultaneously with a similar heap of calcium sulphate (taken as the standard of whiteness) through two long tubes arranged side by side as binoculars, glasses of standard degrees of depth in yellow, blue, and red being interposed in the tube through which the calcium sulphate is viewed until a colour match is obtained. It is thus obvious, from a consideration of the theory of colours, that theoretically not only would it be possible to match the *hue* of a given colour, but in virtue of *subtractive* effect obtained by passing white light

through complete and equal units of primary colours a certain degree of obscuration or units of black may be obtained. Thus, if a given colour were matched by interposing in the calcium sulphate tube units represented by red 1·3, yellow 0·7, and blue 3·0, the effect produced will be equivalent to 0·7 units of black, 0·6 units of red, and 2·3 units of blue. Unfortunately, however, the instrument has not found much favour among workers in pigments, as the difficulty of obtaining colour matches of richly coloured pigments is exceedingly difficult owing probably to fatigue of the eyes. It is understood, however, that for tintings of white, such as would occur in white pigments, flours, pale coloured aqueous extracts, etc., the instrument has been found very valuable. Other methods of colour measurement * have been suggested, but being of comparatively recent introduction, nothing yet is known as to their value in practice.

An important point in connection with the valuation of pigments in regard to their colour arises in their so-called " undertone " obtained on reduction. This undertone often appears as a colour complementary to that which dominates in the pure pigment. Thus, although chrome yellows, yellow ochres, red oxides, and many colours on dilution with white pigments yield colours of lesser *purity* but of similar *hue*, others, such as many lake reds, browns, etc., yield under similar conditions colours of lesser purity dominating in hue. The apparently dead black pigment, vegetable black, yields on reduction greys with a strong blue cast, whilst carbon blacks yield brown-greys.

(ii) *Chemical Effect upon the Medium.* In spite of its many disadvantages, the great popularity of white lead, or basic carbonate of lead, as a pigment is undoubtedly due to its effect upon the medium (linseed oil) in which it is used. It stands by no means at the head of the list of white pigments for either colour (purity of its white), opacity, or cost, yet it is safe to assume that it finds its way into

* Lawrance, *O. and Col. Chem. Assocn.*, 1919, *2*, No. 6; Bawtree, *O. and Col. Chem. Assocn.*, 1919, *2*, 61.

more paints than any other pigment. It being a recognized fact that its basicity is a cause of a slight degree of saponification of the oil medium, it is probable that the small amount of lead soap formed is responsible for the enhanced physical properties of paints of which it is a component. The comparative impermeability of this lead soap is also a probable factor in its extended use.

Among other pigments having decided chemical effect on the medium may be cited those which affect it by reason of their basicity or power to neutralize nascent lower fatty acids (such as formic and acetic acids, etc., from boiled oil during oxidation), and those influencing the oxidation either favourably by virtue of their containing a compound of a metal which acts catalytically as a " drier," *e.g.* certain ochres, umbers, etc., or unfavourably by reason of deleterious impurities. These will be considered under the separate headings of the pigments, although, in many cases, the influence of retardation of oxidation is not well understood.

(iii) *Physical Effect upon the Paint.* An important point leading eventually to marked influences on the behaviour of the paint film on exposure is that of the relative oil absorption of pigments, and will be considered more fully when dealing with the subject of the preparation of paints and enamels. The oil absorption of pigments may be defined as that minimum quantity of oil necessary to convert unit weight of dry pigment from a powder to a definite paste. This constant is conveniently determined in the laboratory by adding raw linseed oil drop by drop from a burette to (say) 10 grams of pigment in a mortar and working in the oil with a powerful grinding action until a completely coherent stiff paste is obtained. The oil absorption of pigments varies from some 6 per cent. in the case of white lead to nearly 200 per cent. in the case of certain smoke-black pigments.

The ultimate physical condition of a pigment, *i.e.* the question of its fineness of division, specific gravity, and electrical charge, which it carries when suspended in a particular medium, or in other words, its approach to or

departure from the colloidal state, has a very great bearing on its employment in paints, and even more so in enamels. To cite the case of pigments, which exist in media to a great extent in the colloidal state, there is the case of zinc oxide in enamel media. These latter usually consist of thickened oils or varnishes very rich in thickened oils. The particular combination of actively-basic zinc oxide in a finely divided state, together with oils of moderate acidity and high viscosity, results in a colloid system of very great stability. Thus, separation of pigment from medium, even when diluted with ether, cannot be accomplished by ordinary filtration, and in an experiment by one of the writers, complete sedimentation did not take place in an ethereal dilution in eighteen months, the high-speed centrifuge alone effecting complete deposition with some difficulty. The suspension showed all the attributes of a suspensoid, the Tyndall cone effect being quite marked, and rapid Brownian movement being visible in the ultramicroscope. The suspensoid, moreover, was bluish by reflected, and orange by transmitted light. A "solution" of an intimately ground mixture of linoxyn and Peruvian ochre in amyl alcohol showed the pigment to be in a similar condition.

The colloidal condition of smoke-black in the preparation known as "Indian ink" is well known, the aqueous solution absolutely defying separation of the pigment by the ordinary means of filtration. Perhaps the most perfect case of colloidal suspension is that of Prussian blue in oil. In this case the high-speed centrifuge is quite unable to remove the last traces of suspended pigment.

A property often utilized in pigments and probably intimately linked up with the foregoing, may, for want of a better name, be termed "suspending power." This is well exemplified in the case of China clay, which, although not showing the usual attributes of a colloidally-suspended pigment, is nevertheless capable of preventing deposition to a hard cake in the bottom of the container in the case of paints containing pigments of known high specific gravity and low oil absorption. Common whiting similarly shows this

property, whilst precipitated chalk, which for all practical purposes is of similar composition, does not act thus.

A substance possessing particular form of its particles in the finely divided condition is often useful to secure certain physical characteristics in the dry coating. White lead examined microscopically is to a certain degree crystalline, and this property imparts " bite " or " tooth " to white lead paints, both on application and for the subsequent coat.

The White Pigments

1. **White Lead or Basic Lead Carbonate.**—White lead, often incorrectly termed carbonate of lead, is perhaps the best known and most important of the white pigments. The earliest process of manufacture, that known as the " stack " or Dutch process, is the one which, at all events, until quite recently, enjoyed the greatest popularity, although the time taken and difficulties of manipulation have proved a great incentive to attempts to introduce more rapid and certain methods of manufacture, as will be judged by the extensive patent literature dealing with the subject. In brief, the stack method of corrosion consists in forming a stack of earthenware vessels, each having a false bottom acting as a container for dilute acetic acid or vinegar, and supporting on the ledge formed by the false bottom a roll of thin sheet lead. The stack or battery of pots is then enclosed in a chamber over spent tan or dung for a period of about two months, during which time corrosion of the lead to basic acetate takes place by means of the acetic acid volatilized by the heat of the fermenting organic matter, followed by its conversion into basic lead carbonate by the carbonic acid evolved. The stack is then opened, the corroded grids removed, and the unattacked " blue " lead separated by crushing, washing, etc., the metal-free pigment being dried in the usual way. The main disadvantages of the process are the length of time occupied for corrosion, the danger to the operatives opening the stack, and the liability to contamination by lead sulphide from the sulphuretted hydrogen

evolved from the organic matter. On the other hand, the uniformity of the product in so far as its comparatively amorphous condition, opacity, etc., is concerned, has for long placed the product made by this method in the front rank of excellence.

Many other processes have been devised to shorten the period of corrosion, whilst attempting to retain the fineness of division of the stack-made product.* Although the plant used differs in the individual processes, the operations involved are nearly all alike, depending as they do on solution of either "blue" lead or litharge in nitric, or, more usually, acetic acid, and subsequent precipitation with carbonic acid gas. An interesting instance of a "precipitation" process is that of Bischof, as now carried out by the Brimsdown Lead Co. Ltd., at Brimsdown, near London. In this process litharge is first reduced to the state of the black sub-oxide Pb_2O by means of water-gas obtained by blowing steam through charcoal. This is in order to ensure reduction of any red lead which might exist in the litharge, and which would eventually pass through the processes to the white lead, giving it a pink cast. The sub-oxide is then "pugged" or masticated with water to convert it into the white hydrate, after which it is treated in a large closed wooden vat with a solution of lead acetate and a little acetic acid, carbonic acid meanwhile being pumped in under pressure. The amount of gas introduced is measured and serves to produce a basic lead carbonate of any degree of basicity. The acetic acid, serving only as a catalyst, can be recovered, and is used over and over again for succeeding operations.

Of late years perfection of control has reached such a stage that white lead products made by quick processes compare very well indeed with the stack-made article, and which are far superior from the point of purity of colour.

White lead, although varying somewhat in composition in different samples, approximates to the formula $Pb(OH)_22PbCO_3$. This formula would be represented by

* Hurst, "Painters' Colours, Oils, and Varnishes," 5th edition

a compound containing about 70 per cent. of lead carbonate and 30 per cent. of hydrate, whilst the average of a number of samples approximates to 72 per cent. of the former to 28 per cent. of the latter. Dry white lead comes on the market in the form of a heavy white powder or soft lumps, possessing, according to many authorities, a faint but characteristic odour. It has a specific gravity of 6·6, and an oil absorption of as low as 6 per cent. in some samples, *i.e.* a definite paste can be formed by combination of 94 parts by weight of dry white lead with 6 parts by weight of raw linseed oil. The production of the stiff product, commonly known as white lead "paste" or white lead "in oil," can either be made by directly grinding the dry pigment in oil or by "pugging" or milling the wet pulp as it comes from the filter press with linseed oil, the superior affinity of white lead for oil driving out the water.*

White lead is a pigment of high opacity and fairly good stability. Its great popularity in paints is principally due, however, to its power of combining to a certain extent with the oil medium used, the lead linoleate formed conferring certain physical properties of flow under the brush which are highly esteemed in practice, and a good degree of impermeability to moisture. White lead enters into the composition of many paints as a "base" or starting point on account of its high opacity and comparative stability, many pale-coloured tinted paints being obtained therefrom by addition of small proportions of stainers.

The stability of white lead in paints has formed the subject of much controversy of recent years, no very satisfactory agreement or conclusions having been arrived at. In the writers' opinion, however, this would seem to be accounted for to a very great extent by the fact that too little attention seems to have been paid to the other factors obtaining in the paint under trial, *i.e.* the medium used and its relative amount, as it is obvious that pigmentation or

* The cause of this phenomenon is to be attributed to the lower interfacial tension existing in white lead/oil over that of white lead/water resulting in a diminution of surface energy.

relative proportion of pigment to oil in a given medium beyond a limit, is likely to lead to actual exposure of the individual pigment particles to a certain extent. From the mass of controversial evidence, however, a few definite facts stand out. Of all the white pigments white lead is that which has the greatest tendency to go yellow in the dark. This is not a very serious disadvantage, as the yellowness bleaches out once more when the paint is exposed to a good light. White lead paint is also very susceptible to blackening in an atmosphere containing sulphuretted hydrogen. The majority of observers also seem to agree that on exposure to much sunlight and weather white lead paint films soon lose their gloss and " chalk," *i.e.* the oil medium seems to disappear, leaving the pigment in an unbound chalky condition. This latter is probably due to the catalytic action of the lead as a drier, drying, as already stated, being a reaction by no means ended when solidity of the paint film has once been attained.

Of the numerous other white lead pigments which have engaged transitory attention from time to time may be cited the basic chloride, hydrate, sulphite, etc., the only one which has found anything like a moderate degree of popularity being the basic sulphate.

2. Basic Lead Sulphate or Sublimed White Lead.— This product, as found on the market, varies greatly in basicity, some samples having as low a PbO content as 1 or 2 per cent., whilst others contain up to 35 per cent. The usual method of manufacture is by sublimation of galena, PbS, in a current of air. It is also formed as a by-product in the manufacture of litharge by cupellation, a certain proportion of lead compound being volatilized by the action of the heating gases containing sulphur dioxide. A method of only academic interest consists in the precipitation of the normal sulphate from a soluble lead salt and subsequent grinding of the precipitate in a solution of a caustic alkali, when a definite reaction with increase of temperature accompanies the formation of the basic sulphate. No specific claim for distinction from white lead in properties seems to have been made,

barring, perhaps, the altogether erroneous one of its absence of toxicity. Generally speaking, it may be said that the consumption of basic lead sulphate as a pigment is very limited.

3. Zinc Oxide or Zinc White.—This pigment is made by two different methods, known as the direct and the indirect processes. The former, also known as the French process, consists in burning metallic zinc in a current of air, the zinc oxide or fume being condensed in chambers containing bags. Indirect process oxide is obtained by burning the zinc ore, the product differing from that from the other process by its lesser purity of composition and colour.

Zinc oxide is the whitest of all commercial pigments, ranking slightly behind precipitated calcium sulphate in its purity of colour. Zinc oxide is also the white pigment possessing the highest degree of subdivision, this property making it the most suitable pigment to use in white enamels. Owing to the actively basic nature of zinc oxide, much care has to be exercised in the selection of the medium used in its grinding, a badly-refined oil of high acid value being unsuitable by reason of the stiffening or "livering" which occurs progressively after grinding. The opacity of zinc oxide is equal to or possibly greater than that of white lead, but by reason of its greater oil absorption (15 per cent. as against 6 per cent.) the opacity of a zinc white paint appears less than that of white lead paint on account of the lower pigmentation obtaining in the former (H. Pfund, *J. Franklin Inst.*, 1919, *188*, 675–681). On the other hand, the spreading power or relative area covered by unit weight of paint in the case of zinc white is much greater than with white lead. The stability of zinc white in paint films is good, its higher cost usually being considered as one of the factors mitigating against its displacing white lead. In its favour may be stated its absolute non-toxicity and its power to remain well suspended in paints.

4. Orr's White or Lithopone.—This pigment was first manufactured and patented in 1874 by Mr. J. B. Orr. It is one of the most interesting of the white pigments, and now holds an important position in the paint factory,

where it has practically supplanted every other pigment for use in indoor paints and enamels. Lithopone, also known under a variety of other names, *e.g.* ponolith, lithophone, enamel white, etc., consists of approximately molecular proportions of zinc sulphide and barium sulphate, but in so far that the product is subjected to calcination during the course of its manufacture, small proportions, 1–5 per cent. of zinc oxide are usually present. Lithopone, therefore, has the average composition: ZnS 30·0 per cent., ZnO 1·0 per cent., $BaSO_4$ 69·0 per cent. It is prepared by double decomposition of solutions of zinc sulphate and barium sulphide, the latter being obtained by calcination of barytes with coal or other carbonaceous matter. The precipitate is filtered, washed, and dried, but to increase its density and opacity and to reduce its oil absorption, it is subsequently calcined to a white heat in crucibles in the presence of air-excluding agents, *e.g.* sulphur or ammonium chloride, and finally chilled in cold water. The pigment is then filter-pressed, washed, and dried.

Since more than two-thirds of the pigment consists of barium sulphate, a body of low opacity and low oil absorption, it might at first sight be regarded as a diluent or adulterant, diluting the valuable properties of the zinc sulphide. But inasmuch as the zinc sulphide is precipitated along with the barium sulphate, quite a different product is obtained from that prepared by mixing the two constituents together, and indeed lithopone actually possesses a higher opacity than any known white pigment. It is generally considered that the particles of barium sulphate are adsorbed on the individual zinc sulphide particles, thus giving it enhanced properties over that of its constituents.

Lithopone has a specific gravity about 4·25, and an oil absorption of about 8 per cent. As already stated, it is the most opaque of all white pigments, whilst its staining or "killing" power is considerably greater than that of white lead. It is quite non-poisonous, a property which befits it particularly for use in paints for toys. In addition, it possesses little or no basicity, and it can in consequence be

used without fear of "feeding" with the most acid media; in fact, it is quite stable when used with a medium consisting mainly of rosin. The fineness or subdivision of lithopone is about equal to that of white lead.

The weather resistance of lithopone in paints, however, leaves much to be desired, and present-day practice has practically unanimously condemned its use in paints for outdoor work, failure of the paint film occurring very early. Opinion is divided as to whether this failure is due to vulcanization of the oil in the medium by the agency of the zinc sulphide with consequent progressive loss of elasticity, or oxidation of the zinc sulphide to soluble sulphite or sulphate with resultant disintegration of the film. An important drawback to the use of lithopone, especially where the article coated is exposed to much direct sunlight, is the tendency of many samples to darken under these conditions. This darkening is not permanent, but disappears when the source of light is removed for some little time, only to return on repeated exposure. No satisfactory explanation of this phenomenon has been advanced, but it is recognized that the change, whatever it is, is produced in the zinc sulphide part of the product. Moisture is essential for its appearance, carefully dried samples sealed in glass tubes being quite stable. Many patented processes claim to produce lithopone having no tendency to alter in sunlight, and it is only fair to state that many manufacturers are now producing this pigment without its usual attendant disadvantage. Lithopone finds its principal use in the paint industry in interior paints and enamels and in water-paints (distemper). By far the largest outlet, however, is in the rubber and linoleum industries, its stability at the temperature of vulcanization particularly fitting it for use in the former, whilst its non-reactivity to acid oxidized oil and rosin render it useful in mixing with linoleum cement for "inlaid" work.

The Fillers and Extenders

These are substances used either to adulterate paints for the purposes of cheapness or to confer some special

properties other than that of tinting or opacity. What might at first sight be regarded as coming under the head of adulteration is often necessary, a specific example of which will make the case clearer. Whilst in fine painting work, such as coach painting, the body or thickness of colour applied is not considered when applying that particular coat in which coloration, as distinct from filling or bodying is concerned, the house-decorator needs not only to produce obscuration of his under-ground but to obtain thickness by applying the minimum number of coats of paint. Taking the case of such a colour as lamp-black, chosen in particular on account both of its high tinctorial power, high opacity, and high oil absorption, the use of a pure or "genuine" paint would hardly be practicable where the above case is considered, as either the paint would have such a consistency as to be almost a jelly, or, in the case of a suitable consistency being obtained by low pigmentation, the paint film would be too attenuated. Thus an inert filler, such as common whiting or barytes, is used in order that the physical properties of the paint may approach those of the more normal pigments, the quantity of black pigment employed being merely sufficient to secure adequate pigmentation and opacity.

Another case of employment of inert pigments or extenders is that of the so-called lake pigments. In lake pigments the inert filler takes precisely the same place as the fabric in dyeing, *i.e.* it serves as a base or recipient for the lake, without which the lake would be useless.

Barytes and Blanc Fixe.—These two fillers, although as similar in composition as a natural ore and an artificial product may be, differ greatly in their physical properties. Common barytes consists of crushed heavy spar ($BaSO_4$), which has been levigated or water-floated to free it from coarser particles. In cases where much impurity in the form of iron oxide is present giving the barytes a yellow or reddish tint, it is bleached by treatment with hot dilute sulphuric or hydrochloric acid, the purified product being subsequently washed and dried. The colour of barytes should be carefully attended to when buying, since the

pigment finds one of its principal applications in the dilution or " reduction " of white lead. The writers have found that many samples of apparently pure colour indicating freedom from iron develop yellowness after rubbing with linseed oil and allowing to stand an hour or two, and this test is recommended when a determination of iron is not considered expedient.

The specific gravity of barytes varies from 4·2 to 4·5, and the oil absorption from 6 per cent. in the coarser samples to 9 per cent. in the finest. This pigment is particularly inert, both chemically and physically, there being practically no tendency to pass to any degree into colloidal solution in the medium. Hence barytes should not be used alone with pigments of similar tendency, as settlement to a hard cake in the bottom of the container is likely to occur.

The inactivity of barytes and its low oil absorption places it in the front rank of importance as a diluent of paints, since the majority of these are sold by weight. It is the recognized standard for " reducing " or diluting white lead in the trade, the various reductions being known as No. 1 White Lead, No. 2 White Lead, etc., according to the relative proportions of genuine white lead and white barytes used. Although commonly regarded as nothing more nor less than an adulterant, a moderate proportion of barytes is regarded by many authorities as an improvement to many paints, the crystalline nature of the particles offering a good surface for repainting, whilst films of paint containing barytes suffer less contraction as they age than is the case when pure white lead has been employed as the pigment.

Barytes possesses little or no opacity, and is practically deficient in "killing" power, hence it is possible to " reduce " such pigments as greens with barytes with little loss of purity of colour.

Blanc fixe, or precipitated barium sulphate, differs rather markedly in its physical properties from natural barytes. It is prepared by precipitation of barium chloride by sulphuric acid. Certain samples are liable to be imperfectly washed, when the traces of free sulphuric acid remaining

may have a very adverse influence on the paint into the composition of which it enters, for obvious reasons. The characteristic differences between blanc fixe and barytes are the amorphous condition and finer state of subdivision of the former. These manifest themselves in greater oil absorption (15 per cent.) and a higher degree of opacity. The opacity, however, is so low that the pigment cannot be employed in any capacity than that of an auxiliary one, and it finds its principal application in serving as a base for the striking of dyes to lakes. It has in addition a useful field of application in reduction of pure strong colours such as ultramarine and Prussian blues, when the light-reflecting power or visibility of the hue becomes apparent without manifestation of undertone or production of "muddiness." This property is most probably comparable to reduction of pigmentation in an oil/pigment system without simultaneous reduction in solid matter content, *i.e.* viscosity.

Whiting.—Whiting is a naturally-occurring form of calcium carbonate found as chalk deposits in the south-eastern counties of England. Examined microscopically, it is found to consist of the skeleton remains of various species of *Foraminifera*, a marine organism. Commercial whiting consists of chalk which has been ground and levigated in water. It has a specific gravity of 2·65. Whiting finds little application in oil paints as a pigment on account of its low opacity, whilst its high oil absorption (about 15 per cent.) does not render its use economical as a filler. It finds its principal application, however, when ground to a stiff paste in linseed oil as putty. It also forms a valuable pigment in water-paints, where it appears to function as a pigment of high opacity on account of its difference of refractive index from that of the medium present in the dried film.

A form of artificial whiting known as precipitated chalk, or under its trade term of "barytes substitute," found considerable application during the war when barytes was scarce, and was produced as a by-product from the process of water softening. This precipitated chalk was distinctly

crystalline in structure, of better colour than the natural article, and of rather lower oil absorption.

Alumina or Aluminium Hydrate.—Alumina is prepared by the precipitation of ammonia alum or aluminium sulphate with ammonium hydrate, the gelatinous precipitate being filter-pressed, washed, and dried. It forms a voluminous, white powder, which is exceedingly transparent when mixed with oil. On this account it finds little or no application in paint pigments, its use being entirely restricted to pigments for use in printing inks, where great transparency is desired. It is there used as a base for precipitating coal-tar colours to form lakes.

China Clay or Kaolin.—China clay is a hydrated aluminium silicate corresponding approximately to the formula $Al_2O_32SiO_22H_2O$. It occurs as a disintegration product of the granite rocks of Cornwall in this country. China clay, on account of its high oil absorption and transparency, is of little value as a pigment in oil paints, nevertheless on account of some obscure property of appearing as a water-protected suspensoid when mixed with oil, it not only remains in good suspension, but inhibits settlement of other pigments, *e.g.* barytes, red lead, etc. It is principally used, however, as the main pigment in water-paints or distempers, its function as an electro-negative colloid in aqueous media, the stability of suspension of which is increased in presence of alkalies ($OH^{\cdot}$ anions) befitting it especially as an ideal pigment.

China clay also finds application as a base for the precipitation thereon of coal-tar colours intended for use in transparent oil pigments for printing inks or water-paints.

Silica.—Although this substance can hardly be classed as a pigment, it enters very largely into the composition of many types of paint where its distinctly crystalline structure renders it especially valuable in conferring "tooth" or "bite" to an otherwise smooth or soapy pigment. The most valuable varieties of silica for use in the paint trade are obtained by crushing quartz and fractionating into different degrees of fineness by screening. Silica from quartz is to be distinguished by the wedge shape of

the crystals when examined microscopically. In this condition silica forms an invaluable base in the preparation of wood fillers for filling up the grain of open-grained woods, when the crystals form with the binding medium aggregates possessing great rigidity. Silica possesses little or no opacity when mixed with oil, and its oil absorption varies with its fineness of division.

Yellow and Orange Pigments

Lead Chromates, Lead Chromes or Chrome Yellows.—The lead chromates are obtained by precipitation of lead acetate or nitrate with potassium bichromate. A great variety of tints ranging from a pale primrose to a deep orange-red can be obtained by modifying the conditions of the precipitation. Most of the paler tints contain varying amounts of lead sulphate which must not be regarded as an adulterant but as a necessary adjunct in obtaining the light tone. The preparation of the different tones of chromes: primrose chrome, lemon, middle and orange chromes, and Derby, Persian, and Chinese Reds (*q.v.*) is somewhat complicated and carefully guarded as a trade secret by the manufacturers. In general, it may be stated that the redder tones of chromes are obtained by increasing the basicity of the product.

The yellow and orange chromes are the most important of the yellow pigments, being possessed of a great degree of opacity and staining power. They are very fast to light, and fairly stable in acid fumes, but in common with all lead pigments are blackened by sulphuretted hydrogen. They should therefore be used with caution in admixture with sulphur-containing pigments such as ultramarine. They are not as a rule employed in distemper paints on account of the tendency of the free alkali to change their tone to a reddish hue. The lead chromes are used almost exclusively for the manufacture of green pigments in combination with Prussian blue.

Barium Chromate or Barium Chrome.—This pigment, sometimes known as lemon chrome, is little used nowadays

on account of its low opacity and poor staining power. It has the advantage, however, over lead chromes in its stability to sulphuretted hydrogen.

Zinc Chromate or Zinc Chrome.—This pigment is prepared by precipitation of zinc sulphate with potassium bichromate. It has a pale greenish-yellow colour and possesses relatively little opacity and a lower staining power than the lead chromes. It is valuable, however, in forming a green of particular beauty in combination with Prussian blue, the distinction from lead chrome greens being probably based on its relatively higher staining power than transparency.

Yellow Pigments from Coal-Tar Dyes.—These have little importance at the present day in the paint industry on account of their poor opacity. They are derived from mono-azo dyes, of which Hansa yellow is a well-known type. On account of their stability to alkali they find some application in distempers.

The Yellow Earth Pigments or Ochres.—The yellow ochres owe their colour to the presence of hydrated iron oxide, which is present in the earth in conjunction with silica, alumina, lime, small amounts of manganese, and carbonic and sulphuric acids. Their tone, opacity, and staining powers vary considerably in a manner usually independent of their composition. The colour varies from a bright yellow in the case of ochres mixed in Oxfordshire and France to a reddish yellow in the case of those from Derbyshire, Cumberland, and Peru. The process of manufacture consists of crushing, levigation, and drying.

The palest varieties are found in France, where they are treated in that country and arrive on the market with alphabetical titles supposedly designating their colouring properties, *e.g.* JF, *Jaune fin*, JC *Jaune clair*, JFLS *Jaune fin lessé surfin*, etc. They possess, as a rule however, little opacity.

The West of England mines produce a large amount of ochres of great variety, the characteristic of which, however, is their comparatively poor purity of colour, reduction with

white pigments showing up a dirty reddish or brown cast. The most valuable staining ochres come from the neighbourhood of Siena in Italy, from which certain varieties are exported which yield tints resembling yellow ochres on reduction.

The Irish and South American ochres are characterized by high staining powers of somewhat dull colour, in addition to which their high content in manganese (0·5 to 4·0 per cent.) render their use in high-class paints and enamels somewhat dangerous on account of the progressive oxidizing effect conferred on the medium.

Red Pigments

Mercuric Sulphide or Genuine Vermilion.—These pigments are classified according to their method of preparation as English, French, and Chinese vermilions, but their ultimate composition is not materially affected by their method of preparation, although their physical properties of colour, etc., are thus influenced. The common method of preparation is by combination of metallic mercury and sulphur by heat to form the black sulphide which is then sublimed as the well-known red pigment. Vermilion finds little application nowadays on account of its expense, toxic properties, and tendency to settle out in paint (sp. gr. 8·2). It is fairly permanent, and possesses good body and staining power. Its use is practically restricted to certain special purposes where brightness and opacity are desired, the modern lake pigments having almost entirely superseded it.

The Red Lake Pigments.—The only naturally-occurring bright red pigment being vermilion, recourse has been had to pigments obtained by precipitation of an organic dye on an inorganic base. The dyes employed for this purpose may be classified into two varieties: the naturally-occurring dyes, *e.g.* logwood, cochineal, and those derived from coal-tar products, *e.g.* the so-called coal-tar dyes.

(*a*) *Red Pigments from Natural Dyestuffs.* These

pigments are greatly diminishing in importance of late years owing to their cost in comparison with those obtained from synthetic colouring matters. The only colouring matters of any importance used are those of madder and cochineal, which latter is used to make carmine, carmine lake, and crimson lake. Naturally-occurring madder has now been almost entirely superseded by synthetic alizarine, whilst, with the exception of carmine, which on account of its cost is restricted entirely to use as an artist's pigment, the other lakes prepared by precipitation of cochineal are too fugitive to be of any value in paints.

(*b*) *Red Pigments from Coal-Tar Dyes.* These pigments are produced by the precipitation or " striking " of a water-soluble dye on a base consisting of blanc fixe, white lead, lead sulphate, orange lead, etc., by means of a mordant. The lake thus formed is thus analogous to a dyed fabric. The lakes derived from mono-azo dyes are the more numerous and important from the point of view of pigments. These dyes consist of the " coupling " product obtained by combination of a diazotized amine with a phenol, naphthol, amine, or derivatives of the same. Two of the most important dyes used for the preparation of bright red lake pigments are Lithol Red B and Paranitraniline Red, which are respectively sulphonaphthaleneazo-β-naphthol, and *p*-nitrobenzene-azo-β-naphthol. The former forms perhaps the most important red lake pigment used in the paint trade, and is characterized by a great degree of fastness and insolubility in oil (" non-bleeding "). The paranitraniline reds, although very fast to light and of great brilliance, are liable to " bleeding." Many other important pigments are obtained from dyes, of which the naphthol sulphonic acids are the starting points. Helio Fast Red RL (" Toluidine toner ") a derivative of *m*-nitroparatoluidine-1:3:4, is also an important lake-producing dyestuff, and is one of the fastest to light. (For an account of the mono-azo dyestuffs used in the manufacture of pigments, see Allsebrook, *Proc. Oil and Colour Chem. Assoc.*, 1919, *2*, 14.)

Madder, or alizarine lake, is obtained by combination of

alizarine dyestuff with aluminium hydrate. It forms a deep-red somewhat transparent pigment with a fine blue undertone, and is useful in obtaining shades of maroon and rich purples. It is extremely fast to light, but is apt to retard drying of the medium.

The eosine lakes, or vermilionettes, are prepared by precipitation of derivatives of fluoresceïn with lead or aluminium salts. Although of very bright shade they are very fugitive to light, and it is the practice to minimize their fugitiveness by precipitating the lakes on lead bases, *e.g.* white lead, lead sulphate, or orange lead. They are gradually being replaced by the far more permanent naphthylamine reds.

Derby Red, Persian Red, Chinese Red, or American Vermilion.—This pigment consists essentially of basic lead chromate, the details of preparation of which, however, are jealously guarded as secrets by manufacturers. Their properties resemble those of the lead chromes, but their red colour is dependent on their crystalline form, since they readily revert to orange or yellow pigments by loss of their crystalline structure on grinding. This latter disadvantage, coupled with their coarse structure and somewhat dull colour, results in their comparative unimportance as red pigments. American vermilion, as it is termed in the United States, enjoys a certain popularity as a rust-inhibitive pigment in that country.

The Iron Oxides Reds.—Many of these are naturally-occurring, but with the exception of the pigment known as red ochre, they are also obtained artificially by calcination of yellow ochres, waste iron liquors, ferrous sulphate, etc., whilst bearing a similar appellation irrespective of their method of preparation.

Of the iron oxides, red ochre possesses but little importance. It is a red oxide of iron with a Fe_2O_3 content of about 10 per cent., and small quantities have been mined in Yorkshire.

Indian Red was the name originally given to a very pure form of red iron oxide found in India, but the term is now applied to iron oxides produced by calcination of iron liquors.

Three varieties of Indian Red are recognized in the trade, known as light, middle, and deep. The Fe_2O_3 content varies from about 50–95 per cent. The Indian reds are characterized by a very high degree of opacity and staining power, and in consequence of their careful preparation, are finely divided pigments employed in high-class practice.

Spanish red oxide is a naturally-occurring iron oxide mined in Spain. Being of rather coarse texture, and of fairly low iron oxide content (20–40 per cent.), its use is restricted to coarse red oxide paints for the protection of metal work and generally where fineness is not a primary consideration, such as for "backing" in linoleum manufacture. It is considered by many authorities to be a powerful inhibitor of rust.

Red oxide of iron is a generic term covering the classes of iron oxide of medium Fe_2O_3 content, whether of purely natural origin or obtained by calcination of yellow ochres.

Venetian Red is a name sometimes given to the above-described red iron oxide, but generally speaking, the term is usually applied to artificially-prepared iron oxides produced by heating precipitates obtained by the interaction of ferrous sulphate with slaked lime. They consist, therefore, of mixtures of ferric oxide and calcium sulphate, to which barytes is sometimes added to still further reduce the cost. Venetian Red has a brighter colour than light Indian Red, and possesses a staining power and opacity roughly proportional to its iron oxide content.

Turkey Red, scarlet red, rouge, and colcothar are the purest form of bright oxides of iron obtained by calcination of iron liquors. A few varieties of naturally-occurring oxides found in the West of England pass under the designation of Turkey Red. Turkey Red usually contains from 95–99 per cent. of ferric oxide, and possesses a very high degree of both opacity and staining power. These reds fetch the highest prices ruling on the market for iron oxide reds, and their use is, as a rule, restricted to purposes where very high opacity is needed in a paint or enamel or for use as stainers. In conjunction with madder lake very rich deep

reds are obtained, the high opacity of the iron oxide red compensating for the transparency of the lake.

The red oxides are exceedingly permanent to light and most chemical agencies. When the artificial varieties of the oxides are carefully prepared, *i.e.* free from either lime originating from the precipitant or sulphuric acid left as a residue from decomposition of the sulphate, they are very inactive to the medium. The presence of traces even of sulphuric acid, however, is very deleterious, and often explains the retardation of drying which occurs in paints containing them.

Orange Lead.—Although rarely used directly as a pigment this product is one of the most important bases used for the precipitation of dye lakes. It is obtained by roasting massicot, the oxide of lead obtained by decomposition of white lead, in suitably constructed chambers with access of air. In addition to its slightly more orange tint, it differs from red lead in its higher content of PbO_2, which is obtained by similarly oxidizing litharge, the fused variety of lead oxide prepared directly from the metal. This factor is indirectly of importance in correspondingly reducing the proportion of free PbO, an undesirable constituent on account of its basicity and consequent reactivity with acid media.

Red lead is but rarely used as a pigment alone, its main application being that of an addition to white lead or priming paints for reasons which are not very apparent, but are most probably the result of custom.

Brown Pigments

Raw Sienna is a name given to a class of earth pigments of brownish-yellow colour. The original pigment was found near Siena in Italy, but the pigment is also mined in Devonshire, Cumberland, and in America. Sienna resembles yellow ochre in composition, but does not possess quite the opacity, whilst its staining power is higher. Its use, therefore, is restricted to that of a stainer.

Burnt Sienna.—Burnt sienna, as its name implies, is obtained by calcination of the raw variety. It has an orange-brown colour and in its staining strength resembles raw sienna. Both varieties are quite fast to light.

Raw and Burnt Umbers.—These are distinguished as Turkey umbers and English umbers, the former being mined in Cyprus, and being the most valued on account of its strength and purity of colour. Raw umber varies in colour from a yellowish-brown to a dark-brown, the burnt variety (obtained by calcination) having a somewhat warmer tone. In composition they resemble highly manganiferous ochres, the manganese content reaching as high as 20 per cent. in some cases. The umbers are of good opacity and high staining power, and are quite permanent to light. On account, however, of their high manganese content they must be used with caution. Crude unground umber is used by the oil boiler as a drier for dark-coloured oils, both iron and manganese going into solution in the oil.

Vandyke Brown, Cassel Earth, and Cappagh Brown.—These pigments are naturally-occurring earths found in Germany and Ireland. In composition they resemble umber, but contain in addition a bituminous substance from which they probably derive their colour. Vandyke brown is not very fast to light, and is so transparent that its use is entirely restricted to that of a stainer, in which respect it finds considerable use when ground with either water or oil for conferring a walnut colour to wood.

Purple Pigments

Apart from the lakes obtained from purple dyes, for the description of which the reader is referred to the larger text-books, an oxide of iron of brownish-purple tint is found on the market. This is known as Purple Brown or Purple Oxide of Iron. It is usually obtained by calcination of iron liquors, and when thus made does not differ markedly from deep Indian red. It occurs naturally in the West of England mines.

Blue Pigments

Prussian Blue.—A series of pigments prepared by interaction of alkali ferrocyanides and ferricyanides with ferrous or ferric iron salts are of great importance in the paint trade. The different varieties, which differ in their shades according to the materials used and different conditions of preparation, come on to the market under various names.* Although the generic name of Prussian blue serves to distinguish pigments composed of basic iron in combination with the acid radicles ferrocyanogen and ferricyanogen, the name is often applied to a particular shade and strength of pigment. Chinese blue or bronze blue is considered the finest of these colours, and is distinguished by its bronze cast, which causes it to find much favour in the manufacture of printing ink. Prussian blue is a second grade of Chinese blue. The names Paris blue, Antwerp blue, Berlin blue, Milori blue represent varieties slightly differing in shade from Prussian blue, and are names but little used in the paint trade. Brunswick blue is a reduced Prussian blue, *i.e.* a mixture of Prussian blue and barytes.

The Prussian blues are pigments of a very high degree of staining power, but possessed of little opacity. They are fairly fast to light, but have the curious property of bleaching on exposure to strong light and regaining their colour in the dark. They are resistant to acid fumes, but are decomposed readily by alkalies, changing to the reddish-brown colour of ferric hydroxide. Care must therefore be exercised that they are not used in combination with pigments liable to contain alkali material, such as whiting or China clay. Prussian blues are therefore inadmissible as pigments in distempers.

* Although Prussian blues were formerly produced nearly exclusively from *potassium* ferrocyanide or ferricyanide, the difficulty of obtaining potash during the war led to the preparation of these blue pigments from the iron-cyanogen compounds of sodium. Since a small but definite proportion of adsorbed alkali salt forms an integral part of Prussian blues, the substitution of sodium for potassium is not without effect on the hue of the resulting pigment, the sodium blues falling behind those from the potassium salt in the beauty of their tones.

Ultramarine Blue.—Originally this pigment was obtained from its natural source of *lapis lazuli*, and is stated to be still obtained from this mineral for use as an artist's pigment. It is a very important pigment, and is manufactured artificially in very large quantities by roasting a mixture of silica, China clay, sulphur, sodium carbonate, and sulphate. Its ultimate constitution is not known, and the different varieties which vary considerably in their tone differ in their chemical composition.

Ultramarine is a pigment of exceedingly bright blue colour which varies from a greenish-blue to a deep bluish violet. It does not possess great opacity, and is not so strong in staining as Prussian blue. It is very fast to light and alkalies, but is immediately decomposed on contact with acids with discharge of the colour and liberation of sulphuretted hydrogen. Ultramarine is liable to contain small quantities of free sulphur, and on this account must not be used in combination with lead pigments which give a black sulphide. Ultramarine is occasionally liable to retard drying, probably on account of its free sulphur.

Lime Blue is an inferior variety of ultramarine often reduced with China clay, which is used as the principal blue pigment in distemper. The name was originally applied to pigments prepared by precipitating basic copper with lime, but which, however, are now obsolete.

Green Pigments

Brunswick Greens, of which several tints are made, and sometimes designated as light, middle, deep, and extra deep, consist of a mixture of Prussian blue and chrome yellow. The cheaper varieties are made by reducing the above with barytes. The chrome yellow (lead chromate), when replaced by the more transparent zinc chromate, yields a green of peculiar beauty, which, when combined with yellow ochres, or umber, yield a series of fine olive greens. The Brunswick greens are pigments of high staining power and good opacity, combining the properties of their two constituents.

Chrome Green or Guignet's Green.—This is a hydrated chromium oxide prepared by heating together potassium bichromate and boric acid. It finds its principal application as a pigment for indiarubber as it withstands the temperature of vulcanization and the action of sulphur without losing its colour. It is very fast to light and chemical agencies, but is of too poor a body and too dull in colour to commend itself for use as a paint pigment.

Emerald Green.—This pigment consists of aceto-arsenite of copper, and on account of its poisonous properties is practically obsolete as a painter's pigment. Its principal use is as an insecticide. It is characterized by a very high degree of permanence and high opacity, whilst its bright hue is unequalled by any other pigment.

The Green Lakes have not found any extensive application in the paint industry on account of the superiority of the Brunswick greens. Lakes from malachite green, naphthol green, etc., struck on green earth (see below) are used in distempers on account of the non-resistance to alkali of the constituent Prussian blue in Brunswick green.

Green Earth is a naturally-occurring earth consisting of a hydrated silicate of magnesium and aluminium and containing small amounts of iron. The bulk of it is mined in Germany, but a certain amount is found in this country. It has a dull green colour, and has little opacity or staining power. It is very fine in texture and forms a good adsorbent or base for basic dyes which can be precipitated thereon without a mordant.

Black Pigments

The black pigments used by the painter are, in all cases but one, varieties of carbon black obtained by burning organic substances in an atmosphere deficient in oxygen.

Black Oxide of Iron.—Black oxide of iron, Fe_3O_4, is a naturally-occurring pigment found in ochre deposits in England. Whilst it possesses neither the transparency nor the staining power of the carbon blacks, it finds some

application in paints on account of its comparatively low oil adsorption (about 30 per cent.).

Gas Black consists of a crude form of carbon obtained as a by-product in gas works. It is the poorest of the carbon black pigments and finds but little use in paints. Its main application is in colouring mortar and cement.

Lamp Black and Vegetable Black.—Lamp black is obtained by the incomplete combustion of various oils in specially-constructed chambers. It is graded into high and low qualities by the distance at which the particles are allowed to deposit from the combustion chamber. The finest variety, known as vegetable black, is relatively free from adhering decomposition products of the oil used which would exercise a retarding action of the paint into the composition of which it enters. Lamp black is a very permanent pigment of high opacity and staining power. On reduction with white pigments it gives cold greys.

Drop Black or Frankfort Black.—Drop black, so-called from the practice, now becoming obsolete, of placing it on the market in tear-shaped masses agglomerated by means of a weak solution of size, is obtained by heating twigs of trees, etc., in a closed vessel and subsequently washing and drying the carbonized residue. It is a black of very intense colour, but of a lower degree of strength than the other varieties of carbon blacks. It is rapidly being superseded by vegetable black and carbon black.

Ivory Black and Bone Black.—As its name implies, ivory black is obtained by heating ivory waste in closed vessels in the same manner as drop black. Bone black is the carbonaceous residue from the distillation of bones in the manufacture of bone oil or Dippel's oil, but in many cases the term ivory black is used indiscriminately for both varieties. Ivory black is a black of very intense colour, and is chiefly prized on this account, being little used as a staining pigment.

Carbon Black.—Carbon black is formed by the ignition of American natural gas from the sources in the neighbourhood of Pittsburg, under suitable conditions of limitation of

access of air. It is the purest form of carbon pigment known, averaging from 95–99 per cent. purity. It possesses exceptionally high staining power and opacity, and its use is becoming increasingly extensive. It differs from lamp black in giving warm browns on reduction with white pigments. It is of exceedingly fine texture, and works well either in oil or water, being devoid of either oily or aqueous impurity. It is used for the manufacture of high-class black enamels, where its fineness of texture renders it especially valuable. (Perrott and Thiessen, *J. Ind. Eng. Chem.*, 1920, *12*, 324.)

Paints, Enamels, and Distempers (Water-Paints)

There exists no hard-and-fast distinction between the three classes of products enumerated above, paints and enamels especially being terms somewhat indiscriminately used in many cases for a similar class of product. Distemper or water-paint, also known sometimes by the American appellation of "Kalsomine," differs rather more in its composition, in that the bulk, or sometimes indeed the whole of the fluid portion of the contained medium consists of water. The three classes of product, however, are characterized by the fact that they are designated for use as a decorative as well as a protective purpose, distemper or water-paint, however, possessing little or no protective action for reasons to be entered into later. A more strict definition of the three representative classes of products intended for decorative coverings, however, will be given.

Paint, or "ready-mixed paint," as it is commonly termed, consists of a suspension of a pigment or mixture of pigments in a medium consisting of raw or boiled linseed or other drying oil, the rate of drying of which has been accelerated by addition of a drier, the fluidity having been reduced to a practicable consistency for application by means of a small amount of turpentine or turpentine substitute. The primary object of the contained pigment in paint is to confer the desired colour to, or obscuration of the ground covered. There are, however, certain other characteristics of paint

which warrant its consideration from a standpoint other than that of merely a pigmented linseed oil. In the first place, it is a well-known fact that the film obtained by allowing linseed oil to dry on a surface hardly possesses those qualities of hardness, impermeability, weather-resistance, etc., required to adapt it to serve as an efficient protective coating. The porosity of dried linseed oil has been discussed in another chapter, and the origin of this porosity is most probably to be found, on the one hand, in the intrinsic nature of the film or, on the other hand, in the expansion and subsequent contraction in volume which the film suffers during and subsequent to its setting to a solid. The partial retention of the volume of the film is obtained by the presence of the pigment which acts similarly to the inert matter which is added to various cements. Another point of importance is to be found in the hardening action conferred by the pigment on the film, acting as it does sometimes by chemical action in forming a heavy metal soap (lead linoleate, zinc linoleate, etc.), or merely by physical effect (silica, barytes, etc.). Finally, owing to the two-phase solid-liquid system created, effects of surface viscosity would result in a thicker film being applied than would be possible in the case of the unpigmented medium. Consideration of the attainment of obscuration or decorative effect by the presence of the pigment has been touched upon in an earlier chapter and need not be entered into beyond that arising out of the physico-chemical effects produced by absorption of certain rays by the pigment.* Thus the inhibition of absorption of ultra-violet rays and degradation to waves of longer wave-length has been obtained in coatings intended for aircraft, by the use of aluminium powder.

In actual practice, however, the attainment of the necessary properties of a paint devolves almost entirely on the pigmentation of the medium to a degree necessary to obtain a reasonable opacity, colour, and fluidity (ease of application). Thus, it is obvious that very light pigmentation

* Eng. Pat. 131,641/1918.

with a finely-divided "active," *i.e.* basic pigment, such as zinc oxide, would be sufficient to overcome the porosity due to sub-microscopic pores, whilst the ever-present slight acidity of raw or boiled linseed oil would result in the formation of a metallic soap which would confer an increased hardness to the film. However, pigmentation beyond this stage is always attained in paints, and the limit is bounded by the point at which excessive addition has the effect of leaving the pigment in an insufficiently bound state. This latter condition may be one of several degrees; the first stage of which would be represented by the condition in which the paint film would dry with a surface devoid of gloss ("flat paint"), but with a considerable degree of hardness and resistance to wear. Pigmentation to a further degree, however, would ultimately result in the dried film being in a powdery condition due to insufficient cementing medium. Beyond the degree of pigmentation above referred to as necessary to fill the sub-microscopic pores of the linseed oil film, further introduction of pigment results in diminished impermeability to gases and moisture. This point is borne out by the results of some unpublished experiments by one of the authors. When paint films of different degrees of pigmentation were examined for their permeability to water vapour, it was found that, beyond the point at which drying resulted in a matt coating being obtained, a very great degree of permeability resulted, intermediate degrees of permeability being roughly proportional to increasing pigmentation.*

In practice it is found that the degree of pigmentation necessary in white paints is arrived at by obtaining that balance of pigment to medium when a maximum opacity is produced without impairing more than is necessary the protective action of the film, or, in other words, its impermeability. This latter point is judged by the relative gloss on the dried film since it is obvious that high pigmentation reduces the gloss of the film.

At this stage it is necessary to introduce the subject

* See also A. de Waele, *Proc. Oil and Colour Chemists' Association*, 99, *2*, 13, 106.

of a qualifying factor when referring to " relative pigmentation." In the chapter on Pigments, the meaning of the term *oil absorption* has been explained as that minimum proportion of oil necessary to transform unit weight of dry pigment to a definite paste. Taking as a specific instance two pigments of extreme oil absorptions—white lead and carbon black, having oil absorptions of 8 per cent. and about 250 per cent. respectively—it is obvious that the relative pigmentation of two paints containing, in the one case, white lead, and in the other, carbon black, will to a certain extent be dependent on this factor of oil absorption. Thus, a white lead " ready-mixed " paint containing 30 lbs. of raw linseed oil per 100 lbs. of pigment will be relatively less pigmented, *i.e.* better " bound " with medium than a carbon black paint having the same relative proportions of pigment to medium. A carbon black paint of relatively similar pigmentation to the white lead paint of the composition described would therefore contain considerably more oil although the relationship is not directly proportional to the relative oil absorptions of the two pigments.*

The question of the application of the two systems of uses of pigmented coatings, under their respective designations of paints and enamels, will be dealt with next, in order to show the differentiation between the two products. The classification into paints, on the one hand, and enamels on the other, is more easily grasped when the two classes of products are regarded more as materials employed in different systems of protective decoration than merely as different products. Considering first of all the problem of the protection of a surface, preferably wood, the various factors arising in the finished coating are :—

(i) Obscuration of underground and pigmentation.

(ii) The application of a weather-proof and wear-proof layer to isolate the underground from the destructive influence of weather, abrasion, etc.

(iii) The production of a final layer on the surface of such a finish as to hide the physical imperfections

* de Waele (*loc. cit.*), p. 115.

of the underground, *e.g.* holes, cracks, grain of wood, etc.

In the system of use of paints, all three objects are obtained simultaneously as far as the perfection of the product renders it possible, by repeated applications of layers of paint of nearly similar composition, obscuration being dependent on the use of a sufficient number of layers. The weather resistance and resistance to mechanical wear obtainable is, however, limited by those properties intrinsically found in the medium used, both raw and boiled linseed oil, however, not being very efficient in this respect. The third factor of "finish," depending as it does on the final attainment of a plane, porcelain-like surface, whether glossy or otherwise, is impossible of realization in a paint of the composition referred to, for reasons which will be entered into when discussing enamels. It is necessary to remark, when considering the system of application of paint, that although no actual differences are usually made in the composition of the materials used in the different coatings, in the initial or priming coat a paint of somewhat different physical properties is required. The reason becomes apparent when the first coating is applied to a very absorbent surface, *e.g.* wood. Owing to the capillarity of the wood cells it is necessary to apply a coating which will not only penetrate the grain of the wood to form a "key" for the next coating, but that this coating, once dried, shall not be so reduced in its "binder" or oil medium by capillary attraction of the wood cells that it will powder off. This end is attained by pigmenting the paint somewhat more lightly in order to ensure more available medium whilst reducing the viscosity, or, in other words, increasing the penetrative power by diluting the oil medium more largely with volatile thinner (turpentine or turpentine substitute). A proportion of red lead along with the white lead or other pigment chosen is usually added, with the alleged object of promoting oxidation of the oil deep in the cell layers.

In the system of painting by application of enamels, however, the three desiderata required in the protective

coating are obtained severally by successive application of layers of differing physical properties and composition. The priming or first layer as a rule differs little in composition from that used in ordinary paints, although it must be stated that since enamels are usually sold as proprietary preparations of the different manufacturers and their compositions are not divulged, they allow of more ingenuity being exercised in their preparation with a view to the attainment of a more efficient sealing or " priming " coating. Thus, in the first place, it will readily be conceded that the necessity for obscuration to a degree beyond that necessary for convenience in application in this coating is hardly necessary, whilst, on the other hand, a quick-setting film, drying without a gloss, but leaving a surface with a better " key " or surface for subsequent coating than would be afforded by amorphous pigment particles is desirable. This end is attained by choice of a suitable medium and incorporation therewith of hard-setting pigments, *e.g.* white and red lead, together with pigment possessing good " bite " or " key," *e.g.* silica from crushed quartz. Improvements are also obtained by incorporating with the product substances which reduce the tendency of the heavier pigments to settle in the container, *e.g.* China clay, asbestine, etc.

In the subsequent coats, a layer of sufficient thickness to cover over any imperfections existing in the grain of the wood is required. Here, again, the necessity for obscuration or pigmentation is not paramount, the requirements of a comparatively quick-drying, well-flowing coat of reasonable thickness being of more importance. These objects are obtained by the use of specially-treated media with a degree of pigmentation consistent with moderate porosity. Solidity or hardness of the coating is obtained by choice of suitable pigments usually without regard to their colour. A good solid foundation obtained as above is regarded in practice as the basis of decorative work, a levelling-off to a plane smooth surface being attained by the practice of cutting away surface imperfections with pumice, etc., and

water, leaving a stone-like ground for the application of the succeeding or decorative coats.

Actual pigmentation is produced in the coatings next considered, white being taken under this heading for purposes of convenience. In this coating, neither weather-resistance nor impermeability need be considered, as these requirements need only be present in the final or surface layer. The pigmenting or " colour " coat should consist of a pigment or mixture of pigments of maximum strength (tinctorial power or opacity) ground in a medium which, although not limited in the proportion of drier it contains by any considerations of weather-resistance (excessive amount of driers being detrimental to lasting properties in an exposed film), should, however, not be siccatized to such an extent that any appreciable solution in the final or protective layer occurs. A very fine degree of subdivision of the pigment and drying of the coat to a " flat " finish is necessary, since no surfacing by flatting with pumice, etc., is permissible on account of the comparative thinness of the layer. The point as to the necessity for application of enamel to a " flat," *i.e.* granular or toothed surface, should be emphasized here, as it is a well-known fact that comparatively impermeable coatings, such as glossy enamel or varnish, do not hold or " key " well to glossy undercoats.

The final, or protective, layer merits special consideration. A system of coatings has been described, so chosen that their successive application furnishes practically a continuous layer intimately bound with and extending into the cells of the wood, of such a thickness that the surface imperfections of the ground on which they are applied is completely covered and of a solidity and hardness consistent with the requirements for which the article coated is to be subjected. In addition, a surface layer, has been obtained of a richness of pigmentation only limited by the intrinsic physical properties of the pigments contained in the colour coat. In consideration of the weather-resisting and elastic properties of oil varnishes, it might be concluded that a layer of such would afford the degree of protection against weather and

wear which is required to complete the structure, and such it would prove to be, were it not for the fact that in many colours or schemes of decoration the delicacy of the tints are such that the colour, conferred by the succeeding coat of oil varnish, would be sufficient to destroy the purity of the colour effect desired. At the same time, it must be pointed out, that in the high-class practice of the coach painter, when pale colours or delicate tints are not at issue, finishing by means of varnishes is usually practised.

The use of the finishing coat of glossy enamel, however, finds its main application in the case of the pale and delicate tints referred to, white enamel being an important variety and forming a class of its own. The finishing enamel, therefore, consists of a medium possessing special properties of weather-resistance and flow, pigmented to just such a degree that the natural yellow or amber colour of the varnish is overcome. There are many difficulties connected with the manufacture of such a product which are readily realized when it is considered that of all the white pigments for use in white enamel, pure oxide of zinc alone is suitable on account of its fineness of subdivision and susceptibility to forming to a great extent a colloidal suspension in the medium. Zinc oxide, being a very actively-basic pigment, readily forms combinations with the gum-resins existing in oil varnishes, with resultant increase in viscosity in many cases to a degree rendering such pigmented varnish unsuitable for use. There are, in addition, certain physical desiderata of enamels connected with their flow, on application, etc., which can hardly be discussed here, and which make the manufacture of such products a branch usually left to an expert. In general, however, it may be stated that the composition of glossy enamels lie in the following directions :—

The Medium.—Whilst in ordinary ready-mixed paints the media consist of raw or boiled linseed oil, such products would not possess the necessary physical or chemical properties required in an enamel for finishing. The instability of oxidized raw or boiled linseed oil has already been

discussed, and a consideration of the figures for variation in weight with time show that disintegration of the dry film sets in very rapidly after the maximum increase in weight due to oxygen absorption has taken place.* In addition to this, the comparatively low viscosities, or, rather, the surface tensions of both raw and boiled oil, would not result in that freedom of flow on application of the enamel that is desired in enamel surfaces. Thus, relatively greater stability to atmospheric influences, together with increased viscosity and surface tension, are attained by the employment of a medium in which the oil present is more or less in the form of polymerized molecules. Such would be found in both oil varnishes and linseed oil thickened by heat ("stand oil"). On account of the high acidity of the gum-resin present in oil varnishes, and the basicity of the zinc oxide pigment which is exclusively used for the pigmentation of the best white enamels, a medium consisting wholly or almost entirely of stand oil is to be preferred, as the reaction between the acid resin and the basic pigment, resulting as it does in undue increase in viscosity of the medium, needs to be regulated by further addition of volatile solvent with consequent low volume-concentration of fixed medium in the film applied.

Certain manufacturers, however, employ gum varnishes containing kauri gum for their media, the resin from such having, in contradistinction to others, quite a low acid value after "running" or fusion. Of recent times, processes have been patented for obtaining neutral gum-resins for varnish making by forming glycerin esters of the fused gum-resins,† whilst certain manufacturers have been successful in employing glycerin esters of colophony as substitutes for gum-resins. In general, however, "stand oil" hardened with a small proportion of elastic gum varnish is used, although many products are on the market in which the medium consists of specially-treated "stand oil" devoid of gum-resin. The principal advantage of the media of the pure "stand oil" type is in their need for a lower proportion of volatile thinner

* Cf. pp. 41 and 45. † Eng. Pats. 23054 and 23,055 of 1914.

to attain a similar viscosity when compared with gum-resinous media. This latter factor in the media of the "stand oil" type reacts favourably on the flow of the coating applied, in addition to resulting in a thicker film being obtained after evaporation of the volatile solvent.

The Pigment.—In the case of white or pale-coloured enamels derived from white, the pigment used is exclusively zinc oxide, the porcelain-like effect of the dried coating being unobtainable with any other white pigment for the reasons previously stated. To obtain fair opacity with overcoming of the slight colour of the medium to obtain a pure white, a degree of pigmentation in the neighbourhood of 65–75 parts of medium (free from volatile thinners) to 100 parts of zinc oxide is necessary, a lower degree of pigmentation yielding a poor white and a soft film, whilst a higher degree impairs the gloss and flow of the enamel.

The case of enamels of a colour other than white and tints derived therefrom would require separate consideration for each pigment, and is beyond the scope of this work. Certain general principles, however, hold over the whole range of pigments. Thus, the maximum degree of pigmentation referred to above must not be exceeded. The "activity" of the pigments used needs to be very specially considered, particularly those which have a tendency to accelerate oxidation, since an undue rate of oxidation in a highly glossy film will manifest itself as a loss of gloss due to a microscopic reticulation of the surface owing to volume changes, etc., before any appreciable deterioration of elasticity, etc., takes place. Another cause of loss of permanence in gloss is oil-solubility ("bleeding") of certain lake pigments, notably that of madder. The relatively low opacity or tinctorial power of certain pigments is also a source of difficulty, since the degree of pigmentation has to be maintained strictly within a limit.

The Volatile Thinners.—Little need be considered here in particular relation to enamels. American turpentine is the solvent usually chosen on account of its better properties

of volatility, small distillation range, and solvent action over that of its substitutes. The higher cost need hardly be considered in view of the comparatively low proportion present in enamels.

Manufacture of Paints and Enamels

From the foregoing description of the functions of paints, it will readily be conceded that to obtain those properties of smoothness permitting of their employment in the manner described, the question of efficient subdivision and thorough amalgamation of the constituent ingredients will be paramount. From elementary physical considerations, it will be apparent also that the most perfect amalgamation of solid and liquid phases would be obtainable by minute subdivision of the pigment, this condition favouring the formation of a maximum surface of the latter. Thus, the functions of paint-making machinery are, firstly, that of the obtainment of solid/liquid pastes of as high a degree of dispersion of the former as possible, *i.e.* fineness of grinding, and, secondly, even distribution of the solid phase in the liquid, *i.e.* thorough mixing.

The paint manufacturer proper is not concerned with the business of the preparation of his pigment in a suitable state for grinding into paint, this being the domain of the pigment maker, hence paint makers' pigments arrive on the market in a more or less finely divided condition. The grinding of pigment in the medium, however, has for its object that of the breaking down of agglomerates of fine particles and the isolation of the latter from each other by a skin or layer of medium. Such an effect cannot be obtained even with the finest of pigments by capillarity alone, a considerable degree of pressure being necessary to obtain the effect. Hence, a consideration of the principle underlying the various types of plant used for grinding pigments in oil will show that in every case the effect aimed at is the bringing together under pressure of a thin layer of pigment and medium. Generally speaking, the manufacture of the finished paint from the raw materials,

pigment, oil, and volatile thinner, divides itself into three stages :—

(1) The preliminary incorporation of the solid pigment with the oil to form a paste of pigment-agglomerate with oil. In more modern machinery, the agglomerate is partly broken down in the preliminary stage.

(2) The subdivision of the oil pigment-agglomerate to a finer state. This may be accomplished in one or two stages.

(3) The dilution or thinning of the paste to a fluid paint of workable consistency. It is obvious that it would be

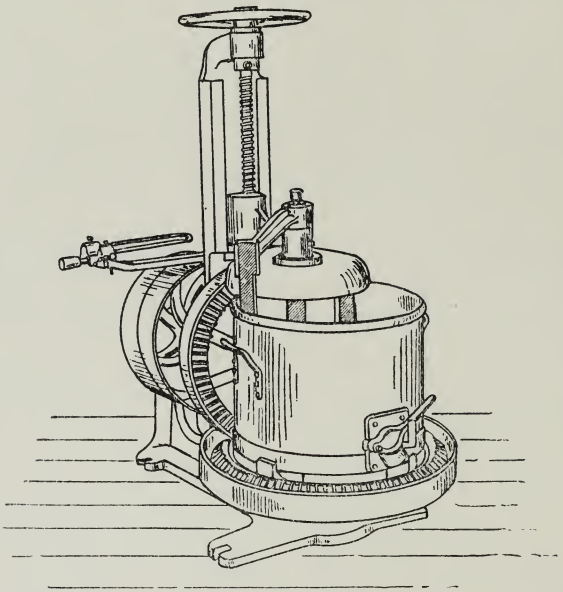


FIG. 16.—Torrance & Sons' " Perfect " Mixer.

inexpedient to perform the actual grinding, as in Stage II., to a fluidity other than the stiffest, if only on account of the lesser weight of material to be treated.

The mechanism of the operations involved will best be understood by reference to descriptions of the machinery.

Stage I.—Preliminary Mixing of the Pigment with Oil. In this stage the mechanism of the process consists in the forcing of the cohesion and capillary attraction between the medium and the pigment agglomerates without, however,

any appreciable subdivision of the latter. In one type of machine for this purpose (Fig. 17), however, some disintegration of agglomerates is inaugurated. In the ordinary old-type pug-mill the dry pigment is charged into the pan, the radial arms disposed about the vertical shaft having their "set" alternately oppositely inclined, thus effecting local compression of oil and pigment particles. A mixer embodying an improvement of the pug-mill principle is shown in Fig. 16. In the pan-mill or positively-driven edge-runner (Fig. 17), the

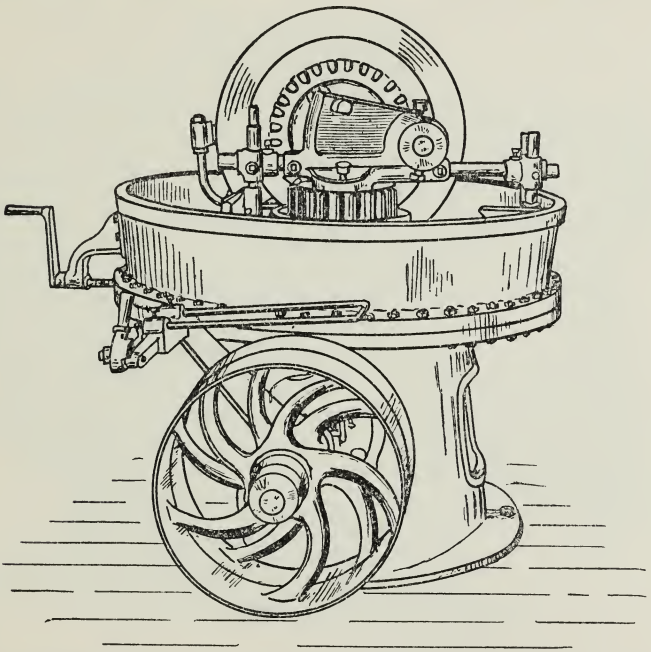


FIG. 17.—Torrance & Sons' Positive-Driven Edge-Runner or " Pan " Mill.

pressing or squeezing action is self-explanatory, and the differential speeding occurring on that part of the periphery of the runner in contact with the material in the bed of the pan is subjected to a slip increasing in intensity from a zero at the middle point of the periphery face to a maximum at its edge, whereby a considerable degree of subdivision takes place.

Stage II.—Grinding. The triple granite roller mill has, in modern times, supplanted every other type of grinding mill for reduction of a pigment-oil mixture to a smooth

butter-like paste, both on account of its rapidity and the perfection of the results obtained. In the Torrance Patent Silent Quadrant Roller Mill (Fig. 18) we have a combination of three granite rollers geared at differential and increasing speeds from back to front (feed to delivery) through quadrants, *i.e.* intermediate spur wheels, enclosed in oil-baths, thus allowing for wear of grinding surfaces without corresponding "bedding" of their respective gears. A lateral motion is imparted to the middle roller by a differential

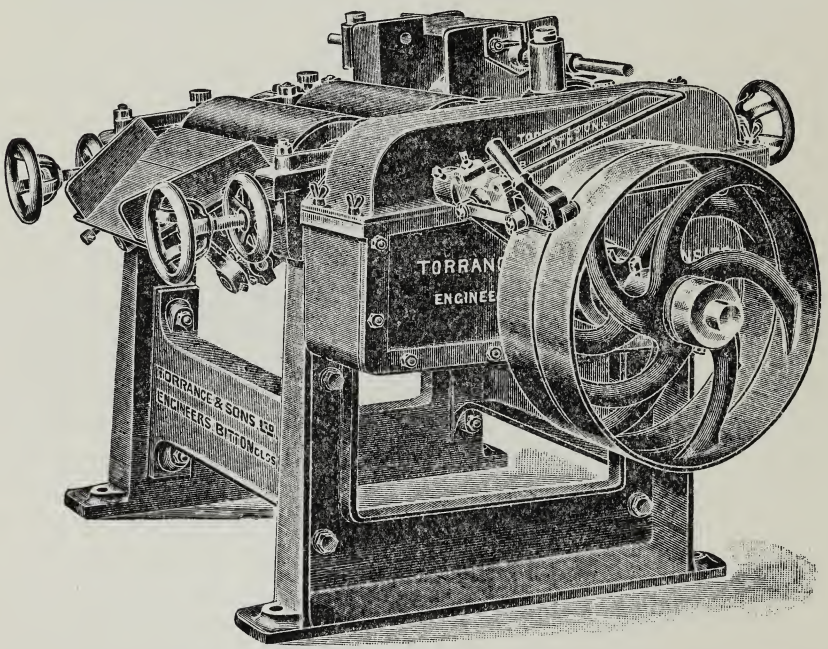


FIG. 18.—Torrance "Patent Silent Quadrant" Roller Mill.

gear similar to that on the rear axle of an automobile, thus ensuring even wear of the rolls and avoidance of ridges. The material from the mixer (Stage I.) is fed by hand or from a hopper on to the back (slowest) roller, whence it travels by contact to the middle, and finally to the front (fastest) roller, a ductor or scraper removing it after treatment. Fig. 19 shows the Torrance Combination Mill embodying the pan-mill automatically delivering to a pair of roller mills in tandem. It is necessary to remark that a

combination of more than three rollers in a roller mill has, in general, not been found expedient owing principally to the resulting overcoming of adhesion by centrifugal force on the delivery roll in consequence of its high speed. It is to be noted that the roller mill described is designed for treating a *paste* as distinct from a paint of workable consistency. This is no disadvantage, since reduction of a *ground* paste to a working consistency is easily accomplished by simple agitation without further

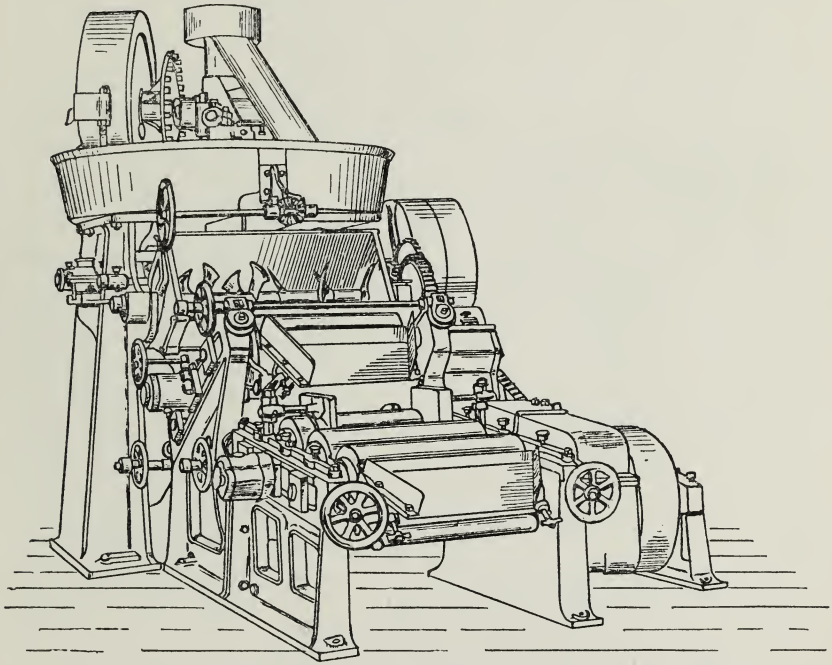


FIG. 19.—Torrance & Sons' Patent "Combination" Mill.

disintegration, and, moreover, such treatment in the paste form is actually advantageous from the point of view of rapidity of output.

For the satisfactory grinding to a stiff paste of pigments in two mutually immiscible media, *i.e.* oil and water, such as obtains in "patent driers," the flat stone mill consisting of two granite discs superposed in a horizontal plane, the lower one being fixed and the upper being revolved, is used. The contact faces of the stones are grooved in order to allow

passage of the material from the centre feed to the delivery at the circumference.

Although the triple granite roller mill has practically supplanted every other type of mill for the purpose, the cone mill (Fig. 20) still finds some favour, mostly for the preparation of small trial batches of paints and enamels, although some manufacturers still retain it under an impression as to its greater efficacy in producing subdivision. In general, however, it may be stated that, apart from laboratory use, its main function lies in the direction of the grinding of pigments in volatile media, *e.g.* spirit varnish paints, pigmented "dopes," etc., where the large surface exposed on the roller mill would be inadmissible. The new "Disc" mill of Messrs. Torrance & Sons (Fig. 21) is an improvement on the cone mill principle, in that both a rotary and an eccentric motion is imparted to one of the grinding surfaces of the granite stones.

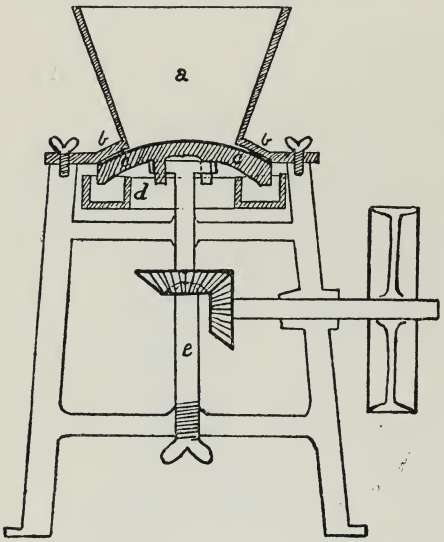


FIG. 20.—Cone Grinding Mill.
(*a*) Hopper; (*b*) Upper Grinding Face; (*c*) Lower Grinding Face; (*d*) Collecting Channel (spout not shown); (*e*) Adjustment.

Stage III. Apart from the consideration of economy and speed of output, the "dilution" of the ground paste paint to the finished product can well enough be accomplished by hand. One type of mixer (see Fig. 16) which has been previously referred to as a mixer for amalgamating dry pigment and medium, is equally applicable for thinning the paste to a working consistency.

The degree of treatment necessary to produce pastes of a sufficient degree of subdivision depends on both the

nature of the pigment and the purpose of the product. An insufficiency of grinding, resulting in the appearance of aggregate particles of larger size than in the bulk, will obviously not have such an importance in a paint intended for the protection of farm buildings, etc., as in that for a glossy enamel. Nevertheless, uniform and fine subdivision, resulting as it does in the presentation of a minimum of

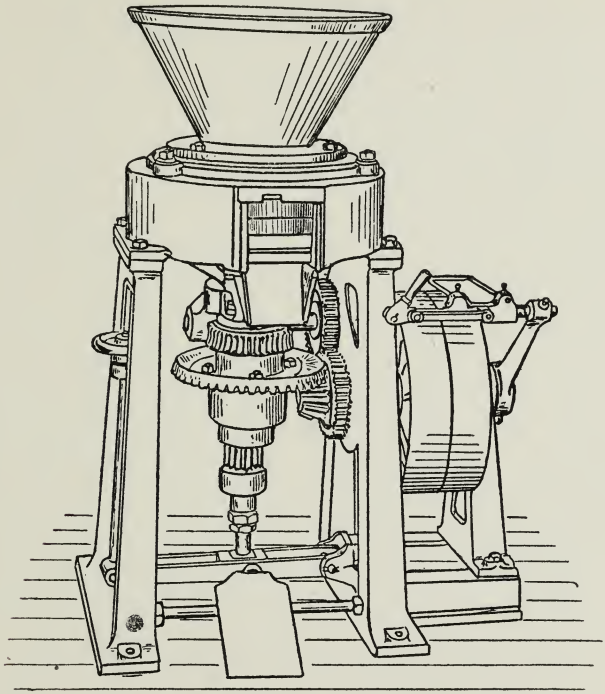


FIG. 21.—Torrance & Sons' Patent "Disc" Mill.

surface for a given area covered, always tends towards more adequate protection.

The manufacture of enamels does not differ in kind from that of paints excepting that the grinding treatment in the former case is always carried to a greater degree, and correspondingly more care is exercised in the manufacture. Since, however, certain types of enamels require grinding in a special medium, often containing an appreciable quantity of volatile thinner, the plant used for grinding must be

chosen with due regard to the minimization of loss of thinner by evaporation. In extreme cases, the cone mill, with its lesser area of grinding surfaces exposed during operation, must be used in place of the roller mill.

Since, as stated above, paints are products intended to perform all the functions desired in a coating, as distinguished from enamels in which each function, *i.e.* filling, priming, undercoating, and finishing, is represented separately over a number of coats, the composition of the former products requires somewhat special consideration. Thus a paint should possess reasonable opacity, tinctorial power, flow, viscosity, and surface tension, and the attainment of all these objects in one product is often a matter of some difficulty. The properties of the common pigments have already been referred to (see chapter on Pigments), so that a recapitulation of the principles governing the choice of ingredients in a paint will be all that need be recalled at this juncture. Without purporting to form any but a very general classification, the subdivision of paints under the headings of their various basic colours will form a scheme for their consideration with regard to the principl es referred to.

White Paints.—Since in pigments of this colour, opacity and staining power, although not synonymous or necessarily of the same order, are always present together, a white paint may consist of one or a mixture of the common white pigments, raw or boiled linseed oil, drier and volatile thinner. The addition of " inert " pigments, other than in a proportion necessary to confer " tooth " or crystalline structure to an otherwise too soft pigment, *e.g.* zinc oxide, must be looked upon as an adulteration. As detailed under " Manufacture of Paint," the paint in its paste form is thinned to a working consistency (" ready-mixed paint ") by means of more oil and volatile thinners. These latter additions must be made with due regard to the physical properties desired in the finished product, too small an addition of oil resulting in a deficiency of flow, whilst too much oil added results in poorness of body, etc. Generally speaking, the amount of thinner in the finished paint is a fixed proportion

relative to the total oil present. The addition of thinner regulates the thickness of the film applied by varying its viscosity. The proportion of drier to be added to a paint will be dependent on the drying power desired and the intrinsic enhancing or inhibiting properties of the pigment.

"Tinted" white pigments, *i.e.* pale tints, are usually prepared by addition of the tinting pigments ground in paste form to the ready-mixed paint.

Red and Brown Paints.—The bright red paints, *e.g.* "Post Office Red," "Signal Red," "Cardinal Red," etc., are obtained by dependence for tinctorial power on the lake pigments (*q.v.*), vermilion finding application only in special cases, owing to certain undesirable properties which it possesses and to its expense. The red lake pigments, however, although of high staining power, possess, as a rule, relatively little opacity, since the majority of them are struck on a transparent base, *i.e.* blanc fixe, alumina, etc. The opacity of these pigments, however, may be increased by precipitation of the dye on a base of high opacity such as orange lead, white lead, or lead sulphate. The employment of lakes precipitated in the latter manner is the expedient usually resorted to in the manufacture of paints, but the presence of lead in the base mitigates against their successful employment in glossy enamels. Increased opacity, therefore, in the latter class of product is usually obtained by employment of a red lake precipitated on a comparatively transparent base in conjunction with a proportion of inert filler such as blanc fixe, having for its object the production of a thicker coating of increased opacity without the corresponding alteration of tone which would be obtained by addition of an opaque pigment such as white lead, etc.

The question of "bleeding" of certain red lake pigments applies rather more in the case of glossy enamels, as the solubility of the organic dye often adversely influences the gloss, rate of drying, etc.

Whilst the production of satisfactory paint and enamel products of bright red colour is one of the most difficult propositions in the paint industry owing to the somewhat

unsatisfactory nature of the dyes at our disposal, the natural and artificial earth oxides offer a wide range of products for the production of paints and enamels of a high degree of fastness to light and good opacity. The staining power and opacity of such a pigment as Turkey Red is of such a high degree that considerable reduction of the same with an inert filler is expedient. Intermediate shades of maroon, purple brown, etc., are obtained by combination of lake reds with iron oxide pigments.

The naturally-occurring and artificially-prepared oxides of iron, having contents of Fe_2O_3 from 10 per cent. upwards, form the basis of the iron oxide paints that are so largely used in the protection of iron structures, their permanence and supposed rust-inhibiting effects making them especially popular in this respect. It should be stated, however, that some varieties of iron oxide reds prepared by ignition of iron sulphate are liable to retard drying of paints, probably owing to their persistent retention of free sulphuric acid and soluble salts. The addition of basic lead chromate ("American vermilion"), zinc chromate, red lead, and zinc oxide to iron oxides is stated to render these paints rust inhibitive.*

Yellow Paints.—The bright yellow paints are almost exclusively prepared from lead chromates. The chromates of zinc and barium are never used alone for the production of yellow paints on account of their relatively low opacity as compared with those of lead. Owing to the unnecessary thickness of coating applied and their high opacity, lead chromates are commonly reduced with inert pigments such as barytes, in the manufacture of paints. They are usually good driers and possess good permanency, excepting in the presence of acid or sulphurous fumes, a failing common to all the lead pigments.

The naturally-occurring ochres place at the disposal of the paint manufacturer a wide range of pigments for the production of paints and enamels of a more subdued yellow than those described above. Some varieties mined in Italy

* Cf. Gardner, "Paint Researches," 1917, p. 116.

possess exceptionally high staining powers and opacities, the tones obtained by their reduction with pigments of high opacity closely simulating those obtained from the chrome yellows. The yellow ochres represent perhaps the most permanent of pigments.

Green Paints.—The various shades of green in paints are almost exclusively obtained by a combination of blue and yellow pigments, the pigment compounds possessing a green colour, *per se*, viz. emerald green and oxide of chromium finding very restricted application for reasons already explained. The brighter shades of green are obtained by combination of lead chromates and Prussian blues, the high opacity of the former and high staining power of the latter particularly fitting the combination as a strong compound pigment. Greens made on such basis ("Brunswick greens") are fairly fast to light, the fugitive component being the Prussian blue, which has a tendency to bleach on exposure to light, the original colour, however, returning in the dark. The duller shades of green, viz. olive green and bronze green are obtained by substitution of chromates of zinc or barium in the one case, and bright yellow ochres in the other, in place of lead chromate.

Blue Paints.—The colour of these paints is exclusively obtained from ultramarine and Prussian blues. Neither pigment possesses a high opacity, and since alteration in tone to a muddy colour results by reduction with opaque white pigments, it is the practice to obtain satisfactory coatings by reduction with inert transparent fillers, the result of which is to increase the thickness of film applied. The intensity of colour (depth or low light-reflecting-power) of these pigments being very great, reduction is always practised, as otherwise the quality of the colour is not apparent. The varieties of ultramarine and ferrocyanogen blues place at the disposal of the paint manufacturer a wide range of tones ranging, in the case of ultramarine, from a greyish-blue to a reddish-purple, and in that of the ferrocyanogen blues from a greenish-blue to a deep blue of pronounced bronze tint. Paints containing much ultramarine blue are often

found to be " bad driers," the precise reason for which is not accurately known, the suggestion of the presence of free sulphur being a popular explanation. Ferrocyanogen blues, however, are good driers, the slight solubility of iron in the medium used being a probable explanation.

Black Paints.—The several black pigments used in paint and enamel manufacture have already been described. The black pigments all possess the general characteristic of comparatively high staining powers when compared with other staining pigments, in addition to which they possess considerable opacity. These characteristics, taken in conjunction with their very high oil absorptions, make it inexpedient to employ them as sole pigments in paints. They are therefore used in conjunction with other pigments. Indeed, their high staining power, generally speaking, is such that it is possible to incorporate quite large proportions of opaque pigments such as white lead into black paints. The high degree of perfection of flow required in glossy enamels makes it necessary to exercise great care in the selection of black pigments for these preparations, the large proportion of adsorbed oily impurities in lamp black having a very adverse effect on the flow and drying properties of an enamel containing it.

Commercial Paints.—When speaking of paints in the foregoing pages, " ready-mixed " paint or paint of a consistency ready for application containing the necessary driers is understood. Nevertheless, the larger users, such as the public bodies, railway companies, etc., are in the habit of purchasing paint in the state of stiff paste, the ultimate users, *i.e.* the craftsmen employing the material, thinning down the paste themselves to a working consistency with oil and thinners and adding the necessary driers. It has already been shown that the necessary grinding takes place entirely in the stage preliminary to thinning, so that such a practice is of no disadvantage to the consumer, and shows advantages in both economy of transport and possibility of storage without loss by evaporation or formation of skins, as driers are usually not present in the paste form

of paint. Such of the coach painting trade as have not adopted the system of decorating by enamels, also purchase paint in the paste form, whereby they are enabled to thin down to a working consistency with any medium they choose.

In regard to flat-drying paints, the ordinary paste paint referred to would be unsuitable, as the proportion of oil carried would be in excess of that which would dry with a matt surface even if the necessary thinner were to consist exclusively of volatile solvent. For such purpose, paste paints are produced in which the grinding medium consists of a mixture of quick-drying varnish (goldsize) and volatile thinner. Such paints are variously known as "turps colours," "ready-bound colours," or "colours ground in turpentine." On account of their deficiency in non-volatile binding medium, care has to be exercised that undue evaporation does not occur, or difficulty would be experienced in subsequently diluting to a thin consistency.

Distempers and Water Paints

When decoration, or more strictly speaking, coloration of a surface without corresponding protection to an appreciable degree is desired, the employment of a distemper or water paint is resorted to. Such cases would arise in, *e.g.* interior decoration of walls, panels, etc. It is obvious that when mere coloration or obscuration of a surface is desired, the question as to the relation between pigmentation and impermeability will not arise in so far as the application of the principle applies to the securing of impermeability. Thus, pigmentation can be carried to a degree only limited by the binding power of the medium, *i.e.* the proportion of medium to pigment in the *dried* film need only be the minimum necessary to secure cohesion. Bearing this fact in mind, it is evident that the problem of the composition of a decorative paint is somewhat simpler than that of one in which impermeability, etc., is necessary, by reason of the important fact that the medium in the dried coating being at a minimum, the influence of closeness of refractive index of medium to that of

pigment (see above, p. 109) in producing lack of opacity will not be so great. To make this clear, we may consider the extreme case of a film of pigment quite devoid of medium. Granting optical discontinuity in the particles of pigments themselves by great subdivision, we have therefore to consider an optical system air/pigment, the low refractive index of the former in comparison with that of the pigment which we may take as being no lower than 1·4,* acting for the attainment of the maximum opacity or optical discontinuity. The increase of opacity taking place as a film of whiting and water dries is thus explained. It should be remarked, however, that in consequence of the fact that such paints contain a proportion of non-volatile medium below that of their *specific absorption*, the dried films obtained therefrom will be devoid of gloss.

The degree of binding medium, *i.e.* the reverse of "relative pigmentation," varies considerably in the several varieties of water paints used commercially. "Limewash" and "whitewash" may be taken as being representative of the lowest members of the class, being merely aqueous suspensions of lime and whiting respectively. "Limewash" is used where disinfectant effect together with obscuration is aimed at, *e.g.* on the walls of cow-sheds, etc. "Whitewash" is used where temporary obscuration of a surface is desired, *e.g.* glass, ceilings, etc. However, neither of these products can strictly bear the appellation of water paints, owing to the absence of binding media in the dried film.

The introduction of a proportion of binder together with an attainment of those properties of increase of viscosity, interfacial (pigment/medium) tension, etc., which characterize a suitable product are in one class of water paint obtained by the use of glue, glue-size, gum, dextrine, or starch. Such a paint results in a more evenly-distributed coating of greater thickness than if water were used alone, and under most conditions obtaining in protected situations, of great permanency. Comparatively little binder is necessary for a large amount of pigment, so that the latter may

* Cf. Gardner, "Paint Researches," 1917, p. 43.

be chosen from a class possessing relatively low refractive indices, *i.e.* whiting, China clay, etc., due regard being had to their colour. China clay (see chapter on Pigments) is largely used on account of its property of remaining suspended in a water medium over long periods. It is obvious, however, that since no change occurs on drying of the paint applied, the dried film will remain soluble in water, thus mitigating against its permanency in damp situations, or permitting of its cleansing by water when soiled.

"Washable water paint," or true distemper, belongs to a class of improved product on that described above. The name is self-explanatory in that these products afford surfaces which are sufficiently bound and water-insoluble to permit of subjection to a mild washing treatment. The insolubility of the dried film is commonly obtained by dependence on one of two principles. In the first, the binder consists of a "solution" of calcium caseinate, or a mixture of casein and slaked lime. Such preparations become insoluble on drying by reason of the transformation of the lime to carbonate, thus leaving the casein in its original (?) insoluble form. This latter class of product owes its popularity to the fact that it is capable of sale in a powder form, addition of water to the consistency desired being all that is necessary to render it ready for use.

The principle of the formation of an insoluble condition of the dried film in the second class is somewhat ingenious, although it is probable that the inception of the product arose empirically without any regard to the main cause of the function involved. These, the most insoluble form of water paint, consist of suspensions of pigments in an aqueous emulsion of glue or alkaline casein solutions with drying oils. The oils are usually present in such proportions as to be entirely kept in permanent suspension and not visibly present in the dried coating. On exposure, the film first dries by evaporation of its water, a secondary reaction of oxidation of the drying oil with evolution of volatile products causing insolubility of the protein material (glue or casein) to take place, and usually completing itself

in 3–4 weeks. It is probable that an aldehyde, *e.g.* formaldehyde, is the agent involved which causes such insolubility. The dried coating becomes then insoluble by reason of both the protecting influence of the water-insoluble solid drying oil and the insoluble form of protein. The presence of drying oil with a refractive index approaching that of whiting and China clay, however, necessitates their complete or partial substitution by those pigments which are commonly used in oil paints (zinc oxide, lithopone, etc.).

Other forms of washable water paints containing emulsifying agents are on the market, *e.g.* sulphonated oils, etc., but their description lies outside the scope of this work.

Little need be said as to the manufacture of water paints. Since the purpose for which they are intended is usually that of the covering of a surface not specially prepared (plaster, brick, etc.), the importance of fineness of grinding is not great, apart from the fact that defects in surface are far less apparent in flat-drying than glossy paints. "Dry distempers," *i.e.* those sold in powder form, are prepared by mechanically mixing and sifting simultaneously through a rotating horizontal sieve. Other distempers are usually sold in paste form and require thinning with water only to bring them to the required consistency. The pigments are then usually incorporated with the media by grinding under an edge runner (see Fig. 17).

It is to be noted that on account of the liability to decomposition which aqueous preparations of glue, casein, etc., are subject, an antiseptic such as phenol, borax, etc., is added to the paste distemper.

Section II.—LINOLEUM, FLOORCLOTH, AND CORK CARPET

Linoleum, together with its sister product, floorcloth, differs from paints and varnishes in its function of serving primarily as a mechanical insulator and decorative coating and not, strictly speaking, as a protective agent against decay and corrosion. Its employment has of recent years assumed gigantic proportions, and on account of its hygienic properties, it is largely superseding carpets, especially for public buildings, shops, etc.

Linoleum was first manufactured a little over half a century ago by Frederick Walton at Staines, and it is curious to note that in spite of the manufacture of linoleum being now carried out in different factories all over the world, little, if any, change in the process of manufacture has been made since its first inception.

The material is too familiar for a description to be given in these pages, but it may be as well to detail the various forms under which linoleum and its congeners are manufactured.

Linoleum consists of a composition of oxidized linseed oil, resins, pigment, wood or cork fibre, mounted on a canvas "backing" usually painted on the under side. It appears in three forms: "plain," *i.e.* unicoloured; "inlaid," in which a many-coloured "tile," floral, or carpet pattern extends right through from the upper surface to the canvas; and "printed," in which a superimposed painted design has been impressed on a plain linoleum. All the varieties agree in that the body of composition is of very definite

thickness, and can be detached as a whole from the canvas.

Floorcloth is merely canvas, such as is used for backing linoleum, with a varying number of coats of coarse paint applied to both sides, the number of applications of paint usually (in the heavier grades) predominating on the face or wearing side. The final face coat invariably bears a printed design.

Cork Carpet is somewhat similar to linoleum in appearance, differing, however, in being far more spongy to the tread and usually rough in surface. It is rarely printed on, or when such is the case, a light design is applied leaving the bulk of the groundwork visible. A further difference in cork carpet is the fact that because wood fibre has an inferior resiliency to cork dust the latter is always used, and the employment of coarse cork ensures such resiliency to a great degree.

Linoleum

As stated above, this product consists of a composition of oxidized linseed oil, resins, cork or wood fibre, and pigment. Linoleum owes its various properties to its several constituents as follows :—

The binding medium consists of oxidized linseed oil, rosin, and kauri gum. The way in which each of these function and their method of preparation will be described later.

The resiliency, and the sound- and heat-insulating properties are due to the cork dust and wood flour, the former being considerably the better for the purpose, but on account of its dark colour it is unsuitable for the lighter shades of inlaid linoleum in any but small proportions without the employment of such a large proportion of " colour-killing " pigment (white) as would diminish its resiliency to too great a degree.

The colour is yielded by the pigment. Cork, when compounded with the binding medium, gives a brown colour.

The "natural-coloured," or brown, linoleums are the most lightly pigmented and consequently possess the greatest resiliency. As resiliency goes hand in hand with specific gravity, those pigments of large volume or low specific gravity are chosen whichever process is employed, the mineral filler or cheapener selected being common whiting to the exclusion of barytes.

Before describing in detail the preparation and employment of the several constituents entering into the composition of linoleum, it will be as well to give a brief note of the sequence of manufacture. On looking at a piece of linoleum, it is evident that the several ingredients have been incorporated during the course of manufacture in a state of greater plasticity than they appear in the finished article. In practice the binding medium is employed in such a state of plasticity that whilst sufficiently solid to maintain temporarily the form given to the intermediate or "green" stage of the product, its adhesion is sufficiently great to ensure the "matured" or finished product being coherent. Relatively little increase in solidity from the unmatured to the finished product is required in linoleum, whilst in floorcloth, which is practically a paint, the article is manufactured in the state of a liquid suspension, becoming transformed when mature to a hard solid similar to a paint film of little resiliency.

The Binding Medium.—Broadly speaking, two methods are in use for obtaining what is the main basis of the binding medium, viz. solid oxidized linseed oil. The first and oldest ("scrim" process) consists in subjecting a film of siccatized linseed oil on a cotton fabric to atmospheric oxidation, the solid oxidized surfaces being successively employed as undercoats for succeeding coats until a thickness of an inch or more is obtained. This oxidation is carried out in "oxidizing sheds," large buildings capable of accommodating 2000 or 3000 cotton fabrics, 20 ft. by 3 ft. in area, suspended vertically and "flooded" with oil by means of an overhead travelling trough. The surplus oil drains into gutters at the base of the building and circulates

for further flooding to the overhead trough by means of a rotary pump (Fig. 22). A thorough flooding is given every twelve or twenty-four hours according to the drying activity of the oil and is continued until sufficient thickness of film is considered to have been obtained. The temperature in the oxidizing shed is maintained a little above the atmospheric in order to accelerate drying. The further treatment of the solidified oil is the same in this and the newer " shower-bath " process to be described.

The more effective " shower-bath " process for effecting solidification proceeds, on account of mechanical expediency,

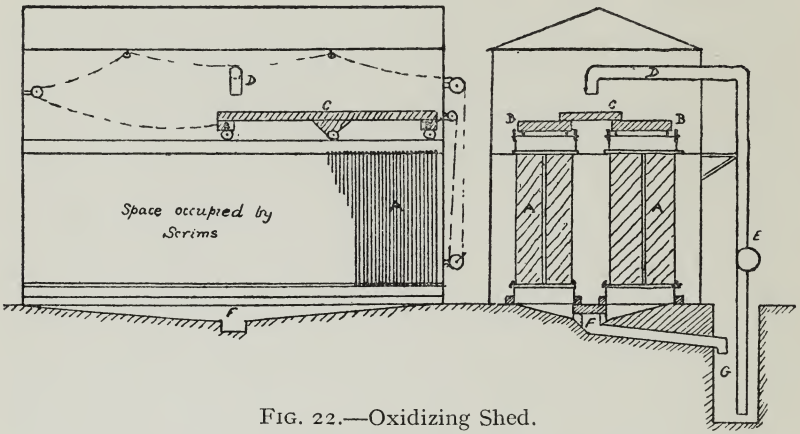


FIG. 22.—Oxidizing Shed.
A, Scrims in rack. B, Flooding troughs. C, Distributing trough. D, Oil pipe. E, Pump. F, Gutter. G, Oil well.

in two stages, the former giving the name to the process. The " shower-bath," as its name implies, consists of a large rectangular box-like chamber, an open-topped perforated-bottomed tank serving as a roof. The bottom part of the box serves as a receptacle for the oil, 10 tons being the usual quantity treated at a time (Fig. 23). The oil, containing an insoluble drier in suspension (usually manganese borate), is run into the lower part of the shower-bath, its temperature being raised to 90° F. or thereabouts by steam pipes lining the sides. It is then continuously pumped over the perforated roof by means of a rotary pump, the oil thereby falling into the chamber underneath in a continual rain. A fan

serves to change the air in the body of the oxidizing chamber as oxygen becomes absorbed and volatile oxidation products are formed. The shower-bath is kept in operation until such time (usually 60–100 hours) as the oil becomes too thick to permit of efficient subdivision of the oil into streams. A graphical representation of the progress of oxidation in the shower-bath is shown in Fig. 24. The continuation of the oxidation process is then proceeded with in another apparatus known as a "smacker." The smacker (Fig. 25) consists of a horizontal jacketed drum fitted internally with rotatory radial arms, of a capacity of about four hundred gallons. The thick oil is run into the smacker, the stirring gear started, steam passed into the jacket until the temperature of the oil reaches 120° F., and common whiting added to the charge to an amount of 5 or 6 per cent. of the oil. A device for circulating fresh air into the smacker is fitted to the body. Once started, oxidation in the smacker proceeds so rapidly that steam is shut off from the jacket and cold water passes in, in order that the temperature may not reach above 120° F. Test cocks at the bottom of the smacker allow of samples being withdrawn at intervals. In about 20–40 hours the oil attains such a degree of oxidation that on cooling it will solidify to a pale yellow, rancid-smelling solid of about the consistency of

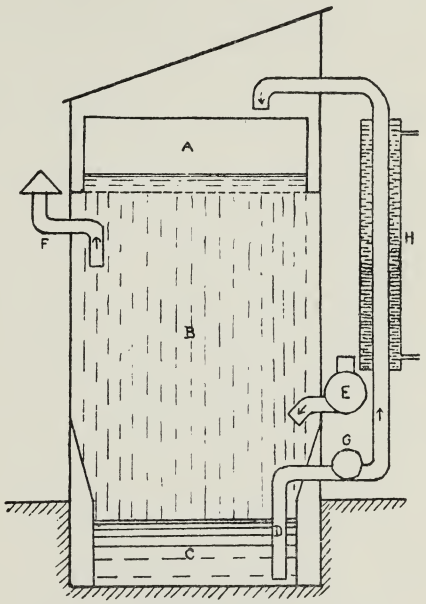


FIG. 23.—Walton "Shower-bath."

A and C, Oil tanks.
B, Oxidizing zone.
D, Oil suction pipe.
E, Fresh air pipe.
F, Outlet for gas.
G, Oil circulating pump.
H, Oil cooler.

common strong size. The " smacked oil " also possesses a slightly honeycombed structure and is almost devoid of greasiness. The honeycombed structure is then developed and the last traces of greasiness removed by warming to about 160° F. in steam-heated ovens for a few days. The effect of the whiting is not very clearly understood, but it is possible that it serves the twofold purpose of forming a calcium soap of the lower fatty acids formed by oxidation and thereby

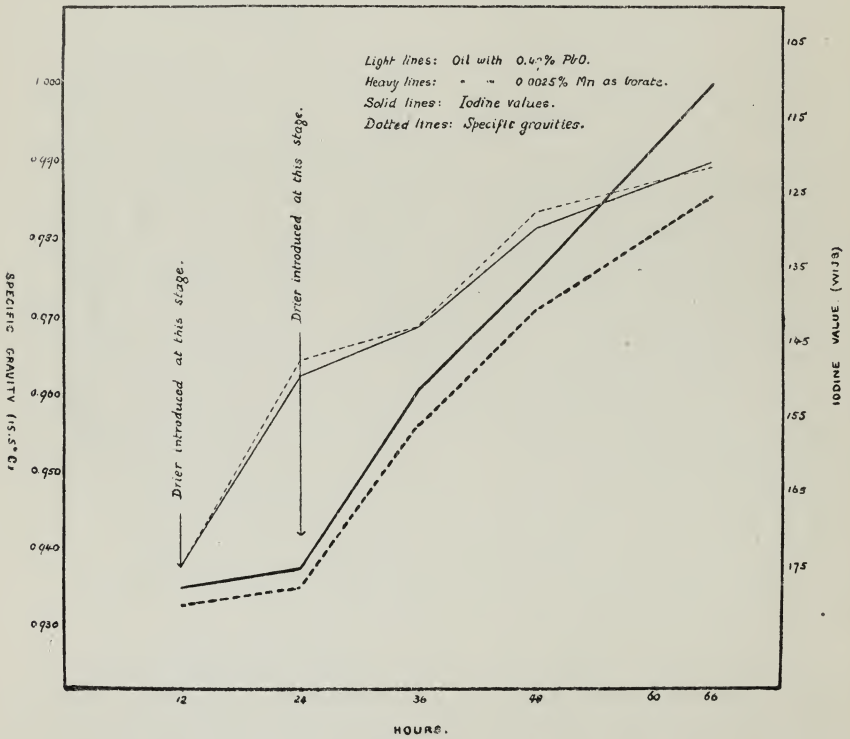


FIG. 24.

diminishing the tendency to undue development of heat by reason of the inhibiting effect of such soap, and also neutralizing the fatty acids formed which would otherwise cause the finished oil to be too greasy. This neutralization would also result in the evolution of carbonic acid, thereby causing the honeycombed structure in the smacked oil. From this point onward in linoleum manufacture, the " scrim " and the Walton " shower-bath " processes are identical.

Neither "scrim oil" nor "smacked oil" at this stage possesses the necessary physical properties to permit of their being used as a binding medium. They both possess a certain degree of elasticity, but lack that adhesive quality or binding power necessary to hold together the other ingredients used, viz. cork dust, wood flour, and pigment. To form a medium for amalgamation of these materials it is necessary to obtain a product of properties very similar to unvulcanized rubber in its warm "tacky" stage. To this end the oxidized oil requires to be converted into "cement."

To understand the "cementing" process we must first of all refer to certain properties of the oxidized oil. If a piece of either scrim or smacked oil be cautiously heated to a temperature of 150° C., the solid oil will melt to a thick buttery liquid with evolution of considerable pungent acrid-smelling fumes. On maintaining the temperature, the evolution of gas will cause the melt to rise, the pale yellow colour to deepen to dark brown, and finally the melting-point is raised to such a point that, as effervescence diminishes, the mass will be converted into a tough dark-brown elastic solid of very similar properties to raw indiarubber. In this latter stage the oil is in its optimum condition to serve as a binder for the other ingredients. The addition of other substances during the cementing process is, however, carried out in practice.*

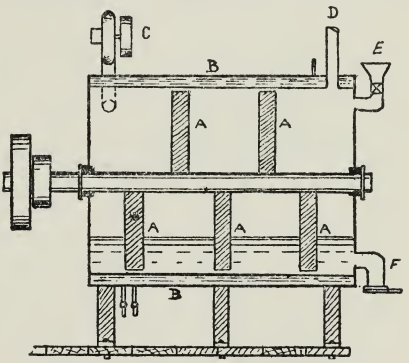


FIG. 25.—Walton "Smacker."

A, Beaters.
B, Water jacket.
C, Air inlet fan.
D, Air outlet pipe.
E, Oil charge valve.
F, Oil discharge valve.

The cementing process is carried out as follows. The cement pan (Fig. 26) consists of a steam-jacketed cast-iron

* For the mechanism of the cementing process and the effect of added substances see A. de Waele, *Jour. Ind. and Eng. Chem.*, 1917, *9*, 6.

pan with a capacity of 200–400 gallons, fitted with either a vertical or horizontal stirring gear and a sluice valve at the bottom. At the top of the pan is an opening about twelve inches in diameter. In the case of the shower-bath process, the smacked oil is added in large pieces weighing about fourteen pounds each, whilst in the scrim process it is considered advantageous to grind the "skins" to a meal through steel rolls in order to disintegrate the contained cotton fabric. Steam is passed into the jacket, the stirrers slowly started, and when incipient fusion of the oil takes place, about 12 per cent. (of the weight of oil) of common rosin in the molten condition is added to the oil, followed by a similar amount of kauri gum dust. The changes detailed above take place as reaction proceeds, and excessive rising is checked by increasing the speed of the stirrers. As "bodying-up," *i.e.* increase of melting-point, takes place, the workman in charge of the process judges the point at which to discharge the contents of the pan and thereby arrest reaction. Towards the end of the process, reaction proceeds very rapidly and some considerable experience on the part of the charge hand is needed, as both under- and over-cementing are equally fatal to the production of a successful cement. A prompt arrest of the reaction is facilitated by either tipping the contents of the cement pan on to the apex of a mound on a concrete floor or preferably by discharging the contents into a hopper leading to water-cooled rolls and thence into separate trays where cooling takes place comparatively rapidly.

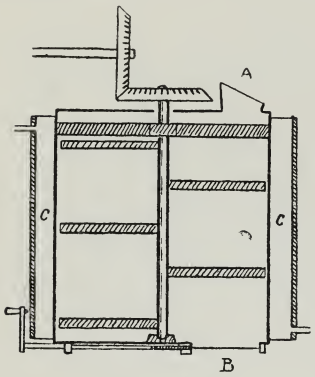


FIG. 26.—Diagrammatic Representation of a Cement Pan.

A, Charging hole.
B, Discharging valve.
C, Steam jacket.

The preparation of the sheet consists subsequently in mechanical treatments, the variations of which are adapted to the several varieties or patterns required. "Plain"

linoleum is the variety which demands the simplest treatment and indeed represents in its mode of manufacture the preliminary stage in the manufacture of all the varieties.

The amalgamation of the cement, cork dust (with or without wood flour), pigments, and filler (whiting), is carried out in steam-heated mixers, the final formation of the sheet being obtained by passing the well-mixed compound through a pair of rollers slowly revolving at different speeds. The thickness of the sheets obtained is determined by adjusting the " set " or distance apart of the rollers. The rolled sheet is detached from the rollers by a " doctor " or scraper. One roll is internally steam-heated whilst the other is water-cooled, this arrangement resulting in a polished face to the linoleum being obtained and facilitating its easy detachment by the " doctor." In the case of plain linoleum, the " linoleum mass " is fed between the rolls with the jute or canvas support, so that the material leaves the rolls on this support.

The remaining treatment of the " cloth " is the same whichever variety is manufactured. The canvas backing on the " green " or unmatured cloth is next coated with a layer of a cheap yellow ochre or red oxide paint backing. The cloth travels canvas side upwards over rollers, and in a nearly horizontal position receives in its passage a pool of paint, which is spread as evenly as possible by a trowel, the excess being removed as it leaves the backing machine by means of a hot roller or " doctor." The composition of the paint is such that it requires melting in a steam-heated pan for use and solidifies to a solid non-tacky coating on cooling on the canvas.

The final process consists in maturing the " green cloth " in large buildings internally heated by steam pipes to a temperature of 140°–160° F. until deemed to be of sufficient hardness to withstand wearing, after which the rough edges are trimmed off so that the cloth is of standard width.

In printed linoleum the " green cloth " is painted on its face by either machine or hand. In either case the paint

is applied by means of a wooden block toothed in parallel ribs about fourteen to the inch, its outline being cut to the shape desired. The paint is picked up from a pad and transferred to the linoleum by pressure, the properties of the paint being such that a perfect surface results with the obliteration of rib marks without undue flowing occurring after the cloth has left the printer, and is hung up for maturing in a vertical position. In hand printing, it is the practice to apply successively the different colours forming the pattern in the portion of the cloth under printing treatment.

There are several varieties of inlaid linoleum made, the oldest consisting in building up the multi-coloured pattern from "green linoleum" in a condition of meal or granules. A grid, cast to a pattern corresponding to the design required, is laid on a table in a horizontal position, successive stencil plates having openings corresponding to sections in the grid being placed on top, and "meal" of a particular colour chosen to fill such sections is dusted in. In a red, white, and blue pattern, three stencil plates would be required. The arrangement of the pattern being conducted on a sheet of strong greased paper, the stencil is removed, the grid carefully lifted so as not to disturb the loose "meal," and the paper support with its layer of meal pulled along under a hydraulic press, the upper surface receiving a section of the run of canvas destined for its final support (Figs. 27 and 28). It will thus be seen that this linoleum is built up from the back. After pressing, the linoleum is ready to receive its backing, after which the maturing is carried out in the same way as in the case of printed linoleum.

Inlaid linoleum of "carpet," or ragged-edged pattern, is carried out in a very similar manner, the pleasing ragged outline of the colour units being obtained by dispensing with the grid and the building up being carried out from the face instead of from the back.

The newer "Walton inlaids," characterized by the sharp clearness of outline and greater cohesion of the finished product, can only be manufactured from oil made by the shower-bath process, owing to the greater cohesion required

in the intermediate stages of manufacture. In this system

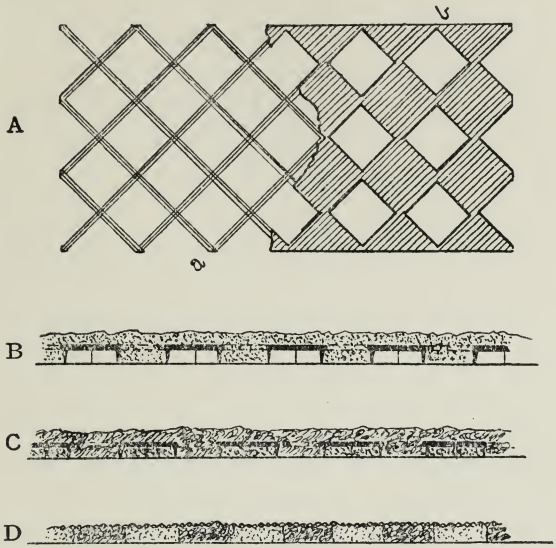


FIG. 27.—" Granular " Inlaying Process.

A, Showing position of stencil (2 colour) on grid.
B, 1st operation showing inlaying of colour No. 1 (section through *a*, *b*).
C, 2nd operation showing inlaying of colour No. 2.
D, Inlaying operation finished, stencil and grid removed; canvas laid; ready for press.

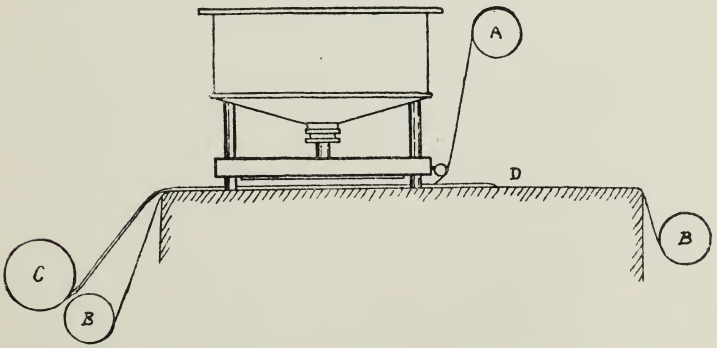


FIG. 28.—" Granular " Inlaying Process. Arrangement of inlaying table with press.

A, Roller carrying canvas.
B, Feed and collecting rolls for waxed paper.
C, Roller carrying finished linoleum.
D, Space for inlaying operation.

of manufacture, sheets of the different colours required are manufactured without the canvas support. The sheets

are then led over rolls fitted with a knife-edged grid, which serves to subdivide the sheet into pieces corresponding in outline to the pattern desired ("solo pattern"), or into smaller units, the subsequent reassemblage of which into local areas similarly serves to build up the desired pattern ("universal type"). The selection of particular units or assembled units for the pattern and rejection of undesired parts is accomplished by means of pistons forming the bases of the knife-edged grids, the pattern being so built up that the units or areas required only are retained within the hollows of the grids, the undesired units being pushed out by actuation of the spring-carrying piston (Fig. 29). After rejection of undesired units, the grid-carrying roller containing the desired units of sheet required is pressed into contact with a large cylinder carrying short pins on its periphery, on to which the units forming that particular part of the pattern corresponding to the colour of the sheet under treatment are transferred. The pinned roller, however, carries also the canvas for the final support of the linoleum, so that after pressing the pinned roller carrying its canvas and adhering units into contact with a pressure roller, the finished linoleum merely requires a final facing before maturing. It is obvious that the number of colours forming the pattern will be limited by the number of differently coloured sheets simultaneously under treatment. A diagrammatic representation of the machine shown in the figure will make the process clear.

Cork Carpet.—The peculiar resiliency of this product necessitates the employment of a binding medium of greater elasticity than that used in linoleum. To this end, oil is prepared in a solidified condition ready to serve as a binding medium without conversion into cement, the use of solidified oil without resins serving further to ensure greater elasticity and resiliency.

The process employed for the solidification of the oil is that known as the Taylor-Parnacott or "Corticine" process. The plant consists of an installation of six iron pots set in a row in a brick furnace. One of the pots has a

capacity of $2\frac{1}{2}$–3 tons, whilst the other five are of half a ton capacity each. The pots are heated from furnaces on the outside of the building in order to minimize fire risk. The

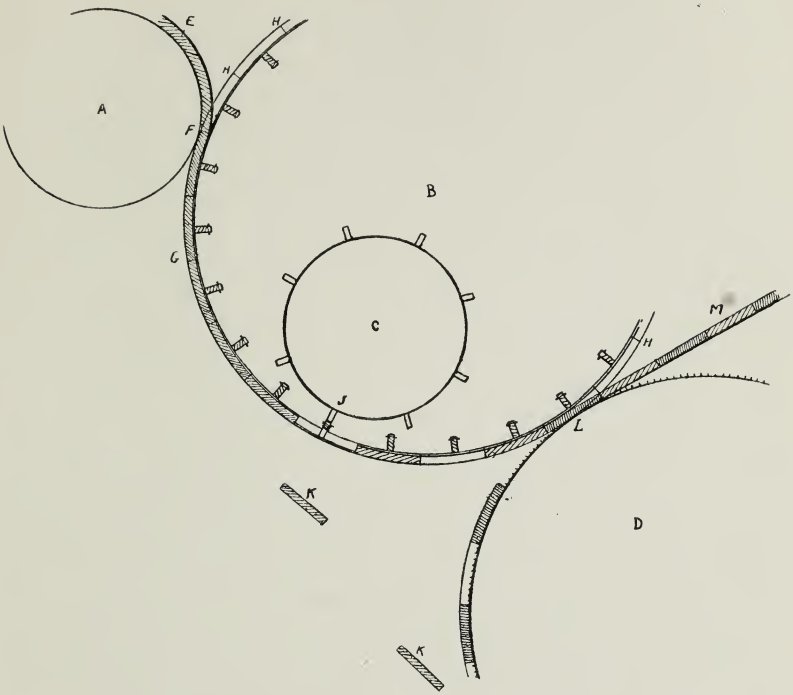


FIG. 29.—Conventional Representation of Walton Machine Inlaying 2-colour pattern.

A, "Cutting Roller."
B, Roller carrying knife-edged grid.
C, "Pattern" roller.
D, Pinned roller.
E, Uncut sheet of No. 1 colour.
F, Cutting operation.
G, Cut sheet of No. 1 colour.
H, Knife-edged grid outlined to pattern.
J, Tappet on pattern roller operating discharge of K, Rejected units.
L, Operation of arrangement of units of No. 1 colour on pinned roller carrying selected units of No. 2 colour.
M, Finished sheet ready for facing.

fire grates consist of flat trucks mounted on wheels and running on a short tramway, whereby temperature may be quickly reduced by withdrawing the grate on its rails away from the flue inlet.

A charge of $2\frac{1}{2}$ tons of (preferably) Baltic oil is run into the larger pot, the temperature raised to about 220° C., and driers, in the proportion of about 1 per cent. each of litharge and lead acetate, added. The function of the latter drier is probably to redissolve any metallic lead resulting from the reduction of the litharge. As soon as the driers are dissolved, a long iron pipe reaching to the bottom of the pot is fitted, and a vigorous current of air passed into the oil by means of an air-pump. The fire is then withdrawn, and blowing is continued for several hours. When moderately cool, the contents of the pot are pumped out and divided equally among the five half-ton pots. The oil in these is then raised to about 250° C. and maintained thereat. After six or seven hours' heating, when signs of incipient solidification show themselves, the oil is well stirred and the fire withdrawn. Complete solidification then takes place somewhat rapidly, and as it proceeds throughout the pot, disengagement of gas within the mass results in the contents of the pot rising to such a point that a series of short cylindrical rings have to be placed round the upper edge of the pot to retain the contents as they rise. Rising to a loaf-like head then ensues and continues several hours, after which a slight contraction occurs. When sufficiently cool, the solid oil is cut away from the sides with a large hay-knife, the centre cut across, and a jet of water run into the bottom of the pot to float out the contents. The solid oil then presents a honeycombed structure in the centre, whilst the bottom and sides are somewhat sticky.

After thorough amalgamation of the sticky "bottoms," dry "middles," and "tops" through mixing rollers, the oil is then ready for direct use as a cement without any further treatment.

The further mechanical treatment is the same as for plain linoleum with the exception that a coarser cork is used and that, owing to the lesser binding power of the Taylor oil, proportionately less cork can be amalgamated. Certain varieties of cork carpet are, after maturing, passed under a sandpapering machine to "buff" the face of the cloth. It

is usual as a trade custom not to apply a painted backing to the canvas of cork carpet.

Floorcloth.—Little description is needed of this product, the use of which is rapidly dying out owing to the vastly superior properties of linoleum. The installation for the manufacture of floorcloth consists, in the case of the machine-made article, of a pair of calendar rollers similar to a backing machine, where canvas is coated both back and front with a coarse paint composed of linseed oil, linseed oil foots, varnish foots and residues, whiting, China clay, and earth oxides, the mass being reduced to a working consistency with white spirit, kerosene, or even water in certain cases. The once-coated canvas is then hung up in drying rooms to harden, after which the coating treatment is repeated until sufficient thickness is obtained. The final treatment consists in the application of a printed design to the face.

In hand-made floorcloth the paint is applied to the canvas held in wooden frames in a vertical position by means of trowels, the treatment being precisely the same as in the machine-made article. Hand-made floorcloth possesses the advantage over the machine-made article in its being capable of being made in much greater widths, six feet or two metres being the usual limit for all varieties of machine-made covering, whilst eight-yard hand-made floorcloth is commonly made.

Floorcloth possesses neither the wearing properties, resiliency, nor the heat- and sound-proof qualities of linoleum.

For further information on the history and manufacture of linoleum the following papers may be consulted:—

W. F. Reid, "Manufacture of Linoleum," *J. S. C. I.*, 1896, *15*, 75.

H. Ingle, "The Examination of Linoleum and the Composition of Cork," *J. S. C. I.*, 1904, *23*, 1197.

M. W. Jones, "History and Manufacture of Floorcloth and Linoleum," *J. S. C. I.*, 1919, *38*, 26.

Part V.—VARNISHES

A VARNISH may be defined as a liquid which dries by exposure to the air to a more or less hard, transparent film, giving protective action or decorative effect to the surface on which it is applied. There are certain exceptions to the transparency of varnishes, notably those known as black Japans, their transparency being only apparent in exceedingly thin layers. Varnishes may be broadly classified into three varieties: (1) those which consist of a medium similar to that of paints, *i.e.* linseed or other drying oils and thinner, the hardness of which may or may not be increased by the addition of certain other substances miscible with or soluble in the drying oil (rosin, gum-resins, etc.); (2) those which consist of a solution of a resin in a volatile solvent; (3) those consisting of a natural product of a tree, drying by enzyme action, *i.e.* Chinese, Japanese, and Burmese lacquers.

Section I.—OIL VARNISHES

These represent the most important of the three classes referred to. For general purposes, oil varnishes may be said to consist of four constituents, drying oil, resin, a volatile solvent, and an accelerator of oxidation of the drying oil. These products therefore "dry" to a hard film by a combination of evaporation of the volatile solvent and an oxidation of the drying oil in its semi-liquid combination with resin. The application of a film or coat of varnish to a surface is usually done with a view to affording protection to the surface against atmospheric destruction, wear and tear, etc., there being exceptions, however, when the main object aimed at is to confer decorative effect by giving gloss and enhancing the beauty of the grain of wood. For either purpose, however, certain of the constituents of oil varnish have the same effect. As stated in an earlier chapter, linseed oil dries to a tough elastic film when subjected to natural atmospheric oxidation. The oxidation product, "linoxyn," confers the elasticity to the film, but neither its hardness, gloss, nor impermeability is sufficient for efficient protective action or the decorative effect desired. The resin (the term embracing both "recent" and "fossil" resins) on the other hand is a body devoid for all practical purposes of elasticity, but of a very hard nature, very resistant to atmospheric effect and therefore stable, of high refractive index and hence conferring gloss. Although the mixture or combination of oil and gum in a varnish has not the same high viscosity as it has after drying or oxidation, the unoxidized liquid is yet of such a viscous nature that it would be impossible of application without the addition of a diluent.

This introduces the question of the volatile solvent. The solvents usually employed are turpentine or "white spirit," the latter representing a fraction of petroleum distillate having a flash-point, mobility, and rate of evaporation more or less approaching to that of turpentine. Other diluents are used, as turpentine substitutes, *e.g.* shale naphtha, shale spirit, petrol, coal-tar naphtha, etc., but on account of unpleasant smell, low flash-point or other objectionable features, they find only a limited application for special purposes. The question of the employment of genuine turpentine, or its most popular substitute "white spirit," has occupied the attention of varnish technologists to a considerable degree in recent years, but without entering into any controversy on the subject, it may be stated that there is little doubt but that genuine turpentine is the best solvent to employ.* Such assertion is based on the facts of the smaller range of distillation of turpentine (the petroleum distillates being at the best but mixtures of hydrocarbons of near boiling-points), its sweeter odour, and its property of absorbing oxygen and thus acting as an oxidation catalyst to a very limited degree. The most important factor, however, is the superior solvent power of turpentine over petroleum spirit.†

The remaining constituent of oil varnishes is the drier or accelerator of oxidation. The mechanism of their action has been referred to in an earlier chapter, but it may be stated here, that of the metals known to possess catalytic action in accelerating oxidation, only the compounds of lead, manganese, and, of later years, cobalt, have found universal use.‡ These driers are introduced into the oil-gum combination either in the insoluble condition as oxides, carbonates, etc., or as metallic salts of a fatty or resin acid. In the former case, the high temperature necessary for the

* See Part III., Turpentine Substitutes.

† Coal-tar naphtha, known as "solvent naphtha" in the trade, has a rather greater solvent power for the usual constituents of a varnish than turpentine, but its noxious odour and toxicity are responsible for its general inappreciation as a turpentine substitute.

‡ See Part II. on Theories of Driers.

saponification of the oil results in more or less darkening of the finished product, so that the metallic "linoleates" or "rosinates" find favour by reason of their solubility at low temperatures.

From the foregoing it will be gathered that for all practical purposes the main constituents of oil varnish are the oil and the resin. The simplest type of varnish would therefore consist of a solution of common rosin in linseed oil with the addition of a suitable drier and reduction to a working consistency with turpentine. Such preparation would indeed constitute a "varnish" and, it is regrettable to state, has in the past found a certain sale with unscrupulous dealers. A consideration of the nature of the non-volatile portion of such preparation, however, will show the poor properties and results to be expected from its use in practice.

In the first place the mere fact of the ease of solution of rosin in linseed oil is such that amalgamation of the two will take place practically at normal temperatures, so that the linseed oil, having received no heat treatment likely to polymerize its glycerides to compounds stable to atmospheric oxidation, will on progressive oxidation show all the disadvantages of instability earlier referred to. In addition to this, it may be pointed out that since polymerization of linseed oil is attended by an increase in its refractive index, the gloss resulting from or conferred by the oil constituent in the varnish will be a minimum. The other constituent—rosin—possesses certain properties (Part III., p. 96) which render it quite unfitted for use as the resinous constituent of a varnish. In the first place, it is decidedly unstable to atmospheric effect, being reactive to oxidation, especially in a thin film, and its oxidation causes a loss in both weight and volume, which latter effect results in a shrinking of surface apparent as cracking of the film. It is stated, moreover,* to yield water-soluble products of oxidation. The low melting-point, low refractive index, lack of toughness

* Paul, *Chem. Rev. Fett und Harz Ind.*, 1914, *21*, 5–8, 36–39, 53–56, 78–80.

and hardness, are further properties contributing to its general undesirability as a constituent of varnish.

In a general consideration of the product, which long experience has shown to be composed of those ingredients which go to make a satisfactory varnish, viz. linseed oil, and suitably treated fossil gum, it can be seen how the necessary properties of the finished varnish are contributed by the ingredients. A preliminary word, however, is here necessary on the subject of the gum-resin or fossil gum. On examining a specimen of a fossil gum such as African Animé, Congo Copal, or Amber, its apparent suitability as a constituent of varnish is at once evident in so far as its brilliance and hardness are concerned. Thus it would seem that the ideal varnish might be obtained were the hardness and lack of elasticity of one of these fossil resins tempered by the influence of linseed oil linoxyn. Unfortunately there is no means whereby such a blending of the properties of these two products can be obtained, as the fossil gums appear to be quite insoluble in or immiscible with linseed oil.* To the high degree of polymerization of the fossil resin is usually attributed its insolubility. However, a solubilizing or depolymerization of the gum, resulting in complete solubility in oil under suitable conditions, is obtainable by a process of partial destructive distillation, known among varnish makers as "running." In this treatment, the solubilizing is attended with partial decomposition of the acids to yield anhydrides or resenes. The solubilized, fused or "run" gum is, however, not recognizable with its original condition, a considerable darkening in colour and some loss of hardness having occurred during the running process. The "run" product, however, will have become by the treatment soluble in linseed oil, whilst the hardness and high gloss conferred on the gum and oil combination will under ordinary conditions of practice bear a direct relationship to those properties existing in the natural product.

To understand the condition in which the several constituents exist, a brief account of the process of manufacture

* Kauri gum is an exception.

will be necessary. A description of the preparation of varnish on a laboratory scale will serve as an introduction to the large-scale process.

The first part of the process consists in the fusion or running of the gum. Small pieces of gum, *e.g.* Congo, broken into pieces the size of peas are sifted free from dust and introduced into a 250 c.c. (tall shape) silica beaker. The gum should not fill more than one-quarter the capacity of the beaker on account of the great amount of frothing which occurs. The beaker is suitably supported and heated over the free flame of a bunsen burner, care being taken that the flame does not play above the height of the gum in the beaker. The first effect of the heat will be to sinter together the individual particles of the gum, the whole then forming a treacly mass, whilst large quantities of terpinoid vapours are evolved. As heating continues, fusion will extend to the rather badly-conducting particles of gum until the treacly mass will have become converted into a viscous liquid. Considerable quantities of gas are evolved, resulting in much frothing and rising of the contents of the beaker, whilst completely-fused gum in the liquid condition will begin to collect as a liquid darker than the unfused gum in the bottom of the beaker. The heat is so regulated and vigorous stirring continued that the maximum rapidity of complete fusion consistent with keeping the frothing under control is obtained. After the lapse of from thirty minutes to one hour, according to the nature of the gum, the contents of the beaker will have become completely fluid, and although the temperature throughout the mass will be higher than at any previous stage in the operation, the head of froth will have considerably diminished. At this point, the appearance of a sample drawn out on a glass rod and allowed to fall back in drops would indicate to a practical "gum runner" the state of completedness of the fusion, as obviously large-scale practice does not permit of inspection through the walls of the metal vessel used. The gum is then ready for the addition of the oil. It is noteworthy to remark at this point that the evolution of gases is responsible for a

loss of from 15–30 per cent. in weight on that of the gum taken, the degree of loss being directly proportional to the degree of fossilization (age) and hardness of the gum. It is also interesting to note that there appears to be a constant figure for each class of gum as representing the minimum loss in weight which must occur before complete solubility of the residue in oil is obtained. Indeed it has been proposed to check the progress of the operation by periodically noting the weight of the contents of the pot during fusion. Too little loss results in partial or even complete insolubility in oil, whilst excessive loss results in loss of hardness and darkening of colour in the finished product.

The fused gum is, however, not soluble in oil with the same facility as is the case with many other products possessing the same range of solubility in differing concentrations; thus, if it be desired in the case instanced to make a varnish consisting of equal weights of gum (unfused) and oil, the addition of the whole of the oil at one introduction with consequent lowering of the temperature would induce a chilling of the gum and its prompt precipitation. In practice, the oil is added in a warm condition, small portions being added until a test spotted on to glass shows a milky appearance on cooling, indicating incomplete union of gum and oil. The temperature is then raised until a test sample shows by its clearness on cooling that complete union of the two is effected, when a further addition of oil is made and so on until the whole of the oil required has been introduced.

The remainder of the treatment necessary to convert this resin and oil combination into a finished varnish is the addition of a suitable volatile diluent to render the product easy of application, and the acceleration of its drying properties by introduction of a drier. The viscous resin-oil compound is removed from the source of heat and allowed to cool to a temperature in the neighbourhood of the boiling-point of the solvent chosen, *i.e.* 160°–170° C. in the case of American turpentine. Addition of the thinner is then made, care being taken that thorough stirring during addition is maintained in order not to chill locally particles of the

product. The quantity necessary will vary and depends not only on the viscosity desired for the finished product, but on the intrinsic degree of viscosity or consistency of the varnish before addition of the thinner.

The acceleration of drying properties in the product is obtained, as already stated, by addition of a compound of one or more of those metals which are used to promote drying properties in oils, viz. lead, manganese, cobalt, etc. The introduction of the same into varnishes may be made by addition of an organic compound of the metal soluble in the finished varnish, *i.e.* lead, manganese or cobalt "linoleates," rosinates, acetates, etc., to the product in the condition described above, *i.e.* after addition of the thinner, or alternatively by causing union of the metallic base of the metal chosen with the gum and oil at an elevated temperature

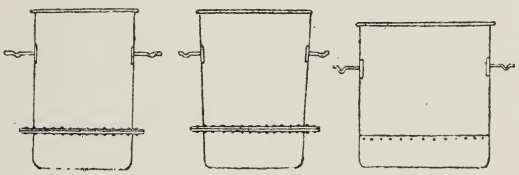


FIG. 30.—Gum Pots.

(*e.g.* 200°–300° C.) before addition of the thinner. In the latter case the base combines partly with any free fatty acid or resin acid present and partly saponifies the neutral glyceride of the oil.

The manufacture of oil varnish on the large scale differs in no material respect from the laboratory-scale preparation described above. The fusion, or "running" of the gum, is carried out in copper or aluminium vessels of 30–100 gallons capacity of various shapes (Fig. 30). The hearth on which the running is carried out usually consists of a hole in the floor of the "making house," beneath which is a grate with a flue running underground constructed in such a way that a very intense bright fire may be obtained and that the products of combustion are completely withdrawn from the interior of the making house. During the "running" process, the contents of the pot are stirred and

examined periodically by means of a stirrer. The making house itself consists of a cement-floored chamber, well illuminated and furnished with as high a roof as possible in order to make contingency for accidental ignition of the contents of the pot. The fumes given off during the running process are led either to a fan or chimney shaft, or alternately a removable cover fitted with a delivery pipe leading to a fan and condenser installation (Figs. 31 and 32).

In practice, the operation of gum-running is usually carried out by two workmen—the " gum-runner " and his assistant. A suitable quantity of gum—usually 112 lbs. in

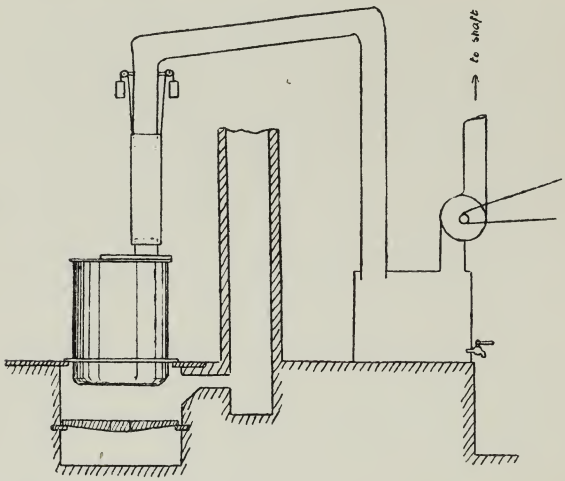


Fig. 31.—Gum Pot with Condenser Installation.

modern practice—is weighed into a clean pot and the latter brought to the fire in the " making house " on a trolley or truck (Fig. 33), occasional stirring being resorted to during the first or sintering stage of the fusion, but as liquefaction of that portion of the gum immediately in contact with the bottom of the pot proceeds, close observation has to be made in order to guard against danger of a sudden rise of the contents of the pot. The temperature of the melt is regulated by bodily lifting the pot off the fire-hole by means of the truck. As the gum approaches complete fusion, more vigorous stirring is resorted

to until finally the gum-runner judges the "run" accomplished. The melt is then ready for "oiling," *i.e.* addition of oil. The requisite quantity of oil is added either by the assistant cautiously pouring it in from a vessel known as a "jack," not unlike a watering-can with an old-fashioned kettle spout, or in more modern practice, the previously warmed oil is pumped up to an overhead tank fitted with a graduated gauge glass marked off in *warm* gallons, from which it is allowed to descend in a thin stream into the gum pot, the contents being meanwhile vigorously stirred. When

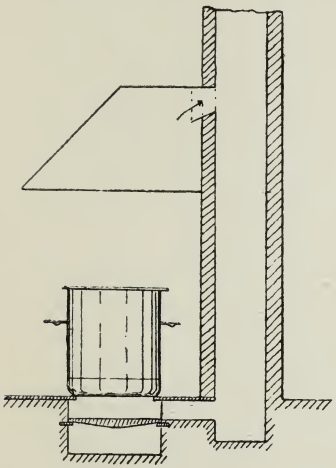


FIG. 32.—Varnish Furnace Installation with Hood to remove fumes.

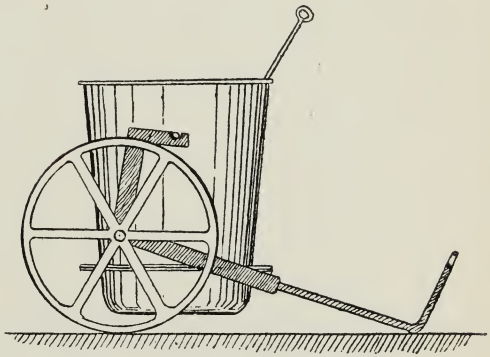


FIG. 33.—Varnish Pot with Truck.

thorough amalgamation of gum and oil has taken place, the gum-oil mixture is ready for addition of the driers.

The rules governing the addition of the driers to linseed oil apply equally in the case of varnish, so that the varnish maker has at his disposal the choice of several metallic compounds in different forms of solubility, etc., in order to produce the effect he aims at in the finished product. To recapitulate, however, we may summarize the *common* metals used as driers in their various forms as follows :—

Class I. driers .. Lead, iron.
Class II. driers .. Manganese, cobalt.

Lead and manganese are usually added in the form of oxides, cobalt being added more conveniently in the soluble condition of rosinate, "linoleate," etc. The use of iron as a drier is considerably restricted by the dark colour of its compounds, but when introduced is usually added as umber (iron and manganese oxides) or Prussian blue.

The distinguishing characteristic of lead when introduced into a varnish is its property of forming an insoluble fraction (lead stearate, palmitate and possibly oleate) which becomes apparent after cooling as a cloudiness which subsequently settles out as a precipitate after a period of weeks to months. Rosinate of lead has less tendency to cause precipitation, and when this occurs, settlement of the "foot" is usually fairly rapid, but the large proportion of lead rosinate necessary by reason of its low concentration in lead militates against its more general use by reputable varnish makers. This applies in general to all rosinates.

Manganese and cobalt have very similar properties in their effect on varnishes in so far that they have a tendency to cause surface drying or skinning in place of a drying right through the thickness of the film. (See under "Defects of Varnishes" at end of chapter.) Both these metals require a very small proportion to accelerate considerably drying of the varnish. The combination of lead-cobalt or lead-manganese is usually resorted to excepting where the presence of the former is undesirable. The use of lead alone in a varnish is not common owing to its rather slow action in this form.

In addition to the method of adding driers to the gum-oil combination, yet another method has found a certain amount of favour with some manufacturers. This consists in the addition of insoluble driers to the finished (thinned) varnish, solution being effected by long agitation in large drums. This method, known as "drumming" or "churning," has the advantage of yielding considerably paler products, probably by reason of the sensitiveness of the metallic soap forming the drier to darkening at the somewhat elevated temperature of solution obtaining in the previously

described method. The agitation with contained air in the drum to which the varnish is subjected also induces a certain amount of bleaching action. "Drummed" varnishes have also the advantage of a lesser tendency to skin over when stored in bulk in open tanks. "Drummed" varnishes, however, require considerably longer periods for clearing than varnishes in which the drier has been introduced at a high temperature.

After introduction of the drier, the varnish pot is removed from the fire and taken either to a cooling room or to the open air, where, after the contents have cooled to a temperature of 160°–170° C., addition of the thinner is made. This operation requires little description, the turpentine or particular substitute chosen being added slowly with continual agitation of the contents of the pot. Addition at too low a temperature may cause precipitation of the gum in certain cases, whilst addition at too high a temperature will obviously occasion losses owing to volatilization.

The varnish prepared as described will, however, not possess the necessary properties which constitute what the skilled user would refer to as a satisfactory product. In the first place, the varnish will hold in suspension the débris of the gum-bark, mineral matter, etc., in addition to which a heavy cloudiness will develop a few hours after the varnish is quite cold. This latter turbidity originates from the same cause as that accruing from ordinary boiled linseed oil prepared with a lead drier, and is caused by the precipitation of insoluble lead soap of the saturated fatty acid constituent of the oil—*e.g.* stearic, palmitic, and myristic acids. On long-continued storage, however, both the débris from the gum and the lead "foot" will settle out, leaving a clear supernatant layer of varnish. Simultaneously with the deposition of "foots," other and more obscure changes will occur, chief amongst which will be a slight bleaching of the varnish. Certain undefined physical changes—probably connected with alteration in the arrangement of the disperse phase in the colloidal solution—will also occur on "ageing," *e.g.* an improvement in the flow under the brush. That

such change can be observed and collated with changes of viscosity has been mentioned in a paper by Seaton, Probeck, and Sawyer (*J. Ind. and Eng. Chem.*, 1917, *9*, 35). It is certain, however, that the more reputable houses manufacturing varnish do not put their product on the market until it has been matured by " tanking " for a period of from six months to two years.

In connection with the general properties of the finished varnish, the influence of the particular volatile solvent employed for thinning should be considered. At first sight, it might appear that little if any influence would accrue from this source, since the presence of such in the varnish film is transitory. Considerable discussion as to the relative merits of turpentine and its more popular substitute " white spirit " has taken place of recent years in technical circles, but it would appear that such has been mainly concerned with questions of odour and relative toxicity of the vapours evolved from the substitute during drying. The question of odour and toxicity, indeed, has been largely responsible for the small popularity of the higher fractions of spirit distilled from coal-tar, *e.g.* naphtha, " tar spirit," etc. From a purely physical standpoint it must be stated in justice to white spirit that from a point of view of flash-point, rate of evaporation, range of distillation, etc., it compares very favourably with the considerably more expensive turpentine, but a point that seems to have escaped criticism is that of the considerably lower solvent power of the petroleum distillates. This point is of considerable importance when dealing with varnishes of the " short-oil " type, *i.e.* varnishes containing less than ten gallons of oil to the 112 lbs. of gum-resin. Such varnishes require considerably more skill in manipulation during thinning, as the relatively unstable combination of gum-resin and oil renders the former very liable to precipitation by careless addition of the inferior solvent. The lower solvent power of white spirit also has an adverse influence on the manipulation of the varnish under the brush, as evaporation proceeds on application, the result being a harshness of flow or " pull " due to partial precipitation.

Varnishes from Tung Oil.—In view of the function which the oil constituent plays as an ingredient in varnish, it is not surprising that considerable attention has been directed to the replacement therein of linseed oil by China wood oil. The greater facility with which a high degree of viscosity can be obtained by heat-treatment and the greater concentration of glyceride having an affinity for oxygen, are properties which strongly indicate the suitability of China wood oil as a constituent of varnish. A further point which has not been touched upon is the nature of the film yielded by polymerized China wood oil on application. Whilst that in the case of polymerized linseed oil never attains a degree of hardness befitting it for use alone as a protective layer suitable to withstand a reasonable degree of abrasion, but requires the presence of hard gum-resins to mitigate against this softness, the oxidation product of polymerized China wood oil yields a film which compares very favourably with that of the linseed oil and gum-resin varnishes. In addition to this it is stated to possess a lower degree of susceptibility to cracking at low temperatures.

From a consideration of its behaviour during heat-treatment, however, the difficulty of arresting the thickening at any desired degree short of production of an insoluble phase, mitigates considerably against its use as sole constituent of a varnish. Similarly, its admixture with gum-resins is a matter of extreme difficulty in view of the high temperature at which it is necessary to effect such incorporation, coagulation of the oil usually resulting. In view, however, of the remarks above as to the intrinsic hardness of the undiluted oxidized China wood oil film, the necessity for the introduction of what is ordinarily understood as a *hard* resin is not so apparent, and advantage may be taken of the lower temperature of incorporation demanded by a soft resin, both to enhance slightly the hardness of the oxidized film and facilitate the manipulation of the oil during heat treatment. It is necessary to remark at this stage that numerous processes have been suggested claiming to permit of the thickening of China wood oil by heat without

production of gelatinization,* but, generally speaking, the claims have not been substantiated, retardation of coagulation being the most that these processes will effect, whilst many depend for their effect on dilution of the tung oil with a difficultly coagulable constituent, the proportion necessary for which deteriorates considerably the property of the film for which pure tung oil is characteristic. In this connection it has been found that a relatively small addition of common rosin to tung oil permits of the desired degree of polymerization being obtained without danger of coagulation when in the hands of a skilled operator. Several advantages are gained by such admixture; the undue rapidity of "setting" (as distinct from the attainment of the maximum increase in weight, *q.v.*) is diminished, and the liability which a varnish from pure tung oil shows to exhibit wrinkles or "webbing" during drying is overcome.

Many variations in product are possible by employing different proportions of rosin and oil and differences of behaviour during drying may be obtained by varying the nature and proportion of drier, etc. It is a significant fact that in spite of the prejudice which the consumer has hitherto had in regard to varnishes containing rosin as their sole resinous constituent, varnishes of this class were found by actual trial over long periods to be the only ones satisfactory for the protection of "doped" fabrics on aircraft, linseed oil and gum-resin varnishes proving quite unsuitable on considerations of permeability, non-adhesion to the glossy "doped" surface and loss of elasticity for long periods under extreme conditions of temperature. Varnishes on a basis of tung oil and rosin have been in use for some time past in the United States, where their resistance to "chalking" (*q.v.*) has formed the main basis for their adoption as varnishes intended for sub-aqueous work.

It may be remarked that the disadvantages attendant on the acidity conferred by rosin in regard to the use of these varnishes as "mixing" varnishes, *i.e.* those intended

* German Pats. 219715/1910; 211405/1908

for use with basic pigments, is overcome by substitution of the acid rosin by " hardened rosin " (alkaline earth rosinates) or " ester gum " (glycerine rosin ester).

The Properties of the Varnish on Application.—In considering the uses to which oil varnishes are put, their main field of application is that of the protection of woodwork. Besides their uses as protective coatings, they have also an important function in the beautifying and accentuating of the natural grain of the wood. This is accounted for by the penetration of the surface cells of the wood by the varnish, thus producing optical continuity with a resultant exaggeration of the darkness of the grain.

From a utilitarian standpoint, however, varnish is applied for the purpose of affording a protective coating against the destructive effects of the atmosphere, moisture, and erosion generally. Thus, it needs to be chemically stable to atmospheric influence (oxidation), physically stable to changes of temperature (elastic), waterproof, and withal sufficiently hard to resist wear. Since it will be readily conceded that in view of the extreme tenuity of the average coat of varnish (about $\frac{1}{750}$ in.), more than one coating will be necessary to give the desired result, and further it will be apparent that one must consider the necessary properties which each coating must possess to fulfil its desired function.

In the first place, a preliminary coating will be necessary to stop the capillarity of the surface cells of the wood and at the same time " set " these cells to a hard rigid layer to obtain a solid foundation. Such effect would be obtained by the use of a varnish of fairly low viscosity to ensure penetration of the cells, but having its gum and oil constituent of rather high viscosity in order that such penetration, once secured, will not go on indefinitely, since a surface sealing of the cells is the only object aimed at. Rapidity of drying will also increase the latter effect. Such a result is obtained by the use of a varnish known as " goldsize." This product constitutes a varnish in which the gum and oil combination has been brought to a viscosity approaching solidity, a liberal addition of volatile solvent then ensuring

a low viscosity in the finished product. The nature and amount of the driers added ensure rapidity of drying. Such a varnish is of limited applicability, possessing as it does little gloss in its dried film owing to its extreme tenuity, low weather-resistance, and slight impermeability, but it fulfils the purposes for which it is designed.

Having now formed a preliminary base or groundwork, the succeeding coats which go to form the protective film proper need next to be considered. From an examination of the properties of the constituents of an oil varnish and of the effect which it is desired to produce, it is evident that from a decorative standpoint it is desirable to obtain as high a finish (gloss) as possible, and to that end the relatively high refractive index of gum-resins will serve in good stead. Thus, for the bodying-up or under-coats, a varnish rich in gum-resin is desirable. The relative hardness of such "short-oil" varnishes furthermore is advantageous from the standpoint of its rapidity of drying and solidity. It is a recognized point from experience that for the application of succeeding coats of varnish, the glossy coat from the preceding layer does not form a satisfactory "key" to the next, and it is the practice to prepare the varnished surface to form a "tooth" or "bite" by removing the excess of gloss. This is performed in practice by the operation of "flatting," which consists in either lightly sandpapering or rubbing down with a piece of hard felt, water, and pumice powder the thoroughly hard and dry surface. Such a prepared surface is to the eye practically devoid of gloss, and examined under a lens exhibits a serrated or toothed surface which is eminently suitable for the successful application of a succeeding coat. It is evident from this that for such purpose to be successfully accomplished in practice, a hard-drying, full-bodied varnish, rich in gum-resin, is necessary. Such varnish constitutes an "undercoating," "preparation," or "flatting" varnish. The relative proportion of gum-resin to oil to form such a varnish is, however, not fixed, several factors contributing to the hardness of the dried film, but it may be stated in general terms that the relative proportion

of gum-resin to oil in this is always decidedly higher than in the varnish for the finishing coat. A further function of the undercoat is to act as an additional cement or binder of the surface cells of the wood.

Having obtained a sufficient body or thickness of varnish, the finishing coating may be applied. In this also many factors have to be taken into account. A coating is required which shall have a maximum of gloss, be of sufficient hardness to withstand the ordinary usage to which the varnished article is to be subjected, and at the same time possess the requisite elasticity to withstand mechanical strain and changes of temperature, in addition to its being both weatherproof and waterproof. On the latter points, it is evident that varnishes intended for exclusive inside use need not possess that degree of elasticity, weather- and water-proofness that are required for outside varnishes.

The question as to the hardness of the dried film is determined by the proportion and choice of gum-resin used in its manufacture. It is evident that the softest of the resins, *e.g.* rosin, would not adequately fulfil such a condition. Elasticity is determined, as referred to previously, by the relative amount of oil present, so that to secure the optimum of these two functions, we should need to employ in our gum-oil combination the *minimum* of the *hardest* gum obtainable. The question of impermeability to water and resistance to atmospheric effect (oxidation beyond the limit necessary to yield a satisfactory wearing film) is, however, a very intricate question, and it is in the obtaining of such results that constitute the art or skill of the varnish maker. The use of China wood oil has placed a valuable adjunct in obtaining impermeable varnishes in the varnish-maker's hands. In connection with stability to atmospheric effect, it is evident that for a given proportion of oil in any two varnishes, since the reaction of the drying or oxidation of a drying oil differs in no way from other chemical reactions, the varnish which dries the more rapidly of the two will first succumb to destruction by atmospheric effect. Since within certain limits, the drying can be accelerated by

increasing the proportion of drier, it is advantageous to restrict the amount added to a minimum to secure a reasonable rate of drying.

When considering the purpose for which a particular varnish is destined, it is important to bear in mind these several contributing effects obtainable from its constituents. As an example, it may be stated that a high degree of elasticity would not be required in a varnish destined for sub-aqueous work, whilst a considerable degree of impermeability to water would be demanded.

Defects of Varnishes

It will be gathered that with such a complex and delicately constituted combination as copal varnish, great liability to defects after manufacture will be present unless control under very strictly regulated conditions is present. Unfortunately, the exigencies of the manufacturing process and our present-day lack of knowledge of the inner mechanism of the reactions involved are such that occasional defects in varnishes present themselves. In addition it is necessary to state that many of the so-called defects of varnish during use may be traced to its application under faulty conditions.

(*a*) **Cracking of the Film, Flaking, etc.**—It may happen that some time after application, the previously elastic film of varnish may progressively harden and lose its elasticity to a point at which with variation in temperature of the surrounding atmosphere, development of cracks takes place. As indicated earlier, the elasticity of a varnish for its specific purpose of use must be carefully considered in that, under conditions favouring the progressive hardening of a varnish film, for example, by exposure to the sun's direct rays, a varnish of maximum elasticity must be employed. The converse, *i.e.* the employment of an elastic varnish intended for exterior use in a situation sheltered from the sun's rays, would, of course, result in a film being obtained of insufficient hardness for reasonable wear. In the case considered, the development of cracks would have

for its origin the presence of too high a proportion of gum-resin to oil, with resultant rapid formation of a film of great hardness and insufficient elasticity under conditions leading to changes in volume, *i.e.* heat and cold. Cracking of the film due to this cause usually manifests itself without any other attendant phenomena. It may sometimes happen, however, that some time after exposure, the erstwhile glossy film takes on a dullness, which when viewed in bright sunlight presents the appearance of an iridescence. This dulling, when viewed under magnification, will resolve itself into a network of fine cracks, which in course of time will develop and extend until they become easily visible to the naked eye. Such destruction of the film has for its origin an oil medium in the varnish of insufficient stability to the progressive influence of oxidation, *i.e.* an oil which has been over-treated with driers. The rapid and progressive oxidation of the oil will result in a rapid loss in weight beyond the point of maximum increase (*cf.* Oxygen Absorption of Oils) with contraction in volume. A somewhat rarer cause of cracking in varnish films originates from the wrongful application of the order of the coatings, *i.e.* the application of the relatively less elastic undercoating varnish on to the finishing varnish. The former, possessing an insufficient elasticity to withstand variations in atmospheric temperatures, results in cracking of the film, an occurrence which is accentuated by the comparative lack of solid support afforded by the elastic undercoat.

(*b*) **"Cissing."**—This term, which would appear to be peculiar to the paint and varnish craft, represents the phenomenon occurring when oil is applied to a damp surface or vice versa, and consists in the contraction or retression of the film applied to separate drops of lesser surface. It thus points for its causation to the high interfacial tension existing between varnish film applied and undercoat, usually dried varnish. " Cissing " usually occurs a few minutes after application of a varnish film to a glossy undercoat that has not been properly " flatted " by pumice

powder, etc., to afford a " key " to the succeeding coat. The manifestation of the " cissing " would appear to be about simultaneous with the period of evaporation of the bulk of the volatile thinner. The cause of " cissing " on an unflatted varnished surface is to be found as before stated in the high interfacial tension existing between the two surfaces brought into contact, while the inhibiting effect of flatting is probably accounted for by the modification of the " angle of contact " consequent upon the toothing of the flatted surface. " Cissing " may also be inhibited by varnishing the undercoat " on the tack," *i.e.* before it is thoroughly hard and dry, when more complete " wetting " takes place owing to slight solubility of the under surface.

" Cissing " may, however, occasionally occur when " flatting " of the undercoat has been done and is then attributable to the use of too new a varnish. The newness of the varnish need not, however, be so great that cloudiness is present, *i.e.* that individual particles be visible. It is probable, however, that microscopic dispersed particles which deposit on evaporation of the volatile solvent act as nuclei similarly charged to the bulk of the medium, and consequent repulsion round the nuclei takes place. The elucidation of the cause of " cissing " is occasionally somewhat difficult, the sweating through of an immiscible constituent from a previous undercoat, *e.g.* some bitumens being sometimes to blame. In very obstinate cases, washing of the undercoat with dilute sodium carbonate solution may rectify the fault.

(*c*) **"Pinholing" or Pitting.**—This phenomenon partakes to some extent of the same nature as " cissing, " and is consequent on the deposition of (generally) visible particles from an insufficiently matured varnish. It may sometimes be due to nuclei of moisture on the undercoat or deposited subsequent to the application of the varnish. When due to insufficiently matured varnish, the remedy is obvious.

(*d*) **"Blooming" and "Chalking."**—These two faults are being treated under one heading notwithstanding their lack of connection, on account of the common misappellation

of the one case for the other. "Blooming," correctly defined, consists in the appearance of a plum-like bloom on the surface of a varnish film, usually a day or two after drying. It generally occurs in relatively inelastic "short-oil" varnishes containing a low proportion of oil, *i.e.* stoving, rubbing, and polishing varnishes, but it also occurs in "long-oil" varnishes and in wood-oil varnishes. Beyond this established fact, there seems to be little concensus of opinion as to its ultimate cause. Many observers, whilst agreeing that its manifestation is restricted to the above-mentioned classes of varnishes, go further in stating that the use of white spirit to the exclusion of turpentine in the varnish is the cause. On such basis, it would appear that the rather poor solvent properties of white spirit for the relatively unstable combination of gum-resin and oil in such "short-oil" varnishes might result in a partial separation of gum and oil with consequent slight optical discontinuity in the film. It has also been suggested* that "blooming" is caused by condensation of moisture on the imperfectly dry varnish film. This suggestion would appear to be substantiated by the fact that such "blooming" may be temporarily removed by rubbing the varnish film with white spirit or by washing with water.† "Blooming" may occur also on varnishes of all types when applied in a damp atmosphere under conditions favouring condensation of moisture on the varnished film. Such may exist when excessive moistening of the floor has been done with a view to the laying of dust during the operation of varnishing. The removal of the bloom formed is often impossible, the only remedy being to remove the coating and to re-apply under favourable conditions.

"Chalking," or the manifestation of a whitish translucence of the film on immersion in water, comes under an entirely different heading. "Chalking" is a fault most marked in elastic varnishes, *i.e.* those rich in oil, but not restricted to them, its intensity on immersion of a varnish

* Seeligman and Zieke, "Handbuch der Lack- und Firnis-Industrie," p. 708.

† *Loc. cit.*

film seeming to be roughly proportional to the relative oil content, and being nearly absent in polishing, etc., varnishes. It is essentially an emulsion phenomenon with water as disperse phase * and is inhibited by the presence of salts in the water. De Waele,† while calling attention to the absence of the phenomenon in films of varnishes rich in China wood oil, suggests that it may be dependent on the presence of suspended water particles, the degree of magnitude of the same, however, being of an order below that of the wave-length of light in this case. "Chalking" disappears on drying off the once-immersed varnish film, the film apparently returning to its original state, but it returns immediately on re-immersion in water.‡ The fault is not one that should be present in varnishes intended for immersion, *e.g.* boat and yacht varnishes.

(*e*) **Wrinkling.**—This, as its name implies, appears as a puckering-up of that part of a varnish film where a thickness has collected owing to flow. With the exception of "short-oil" varnishes, which dry rather by evaporation of solvent than oxidation, it is a fault which will always appear when careless application of the film has been the case. Its cause lies in the fact that contraction in volume in an oil occurs simultaneously with absorption of oxygen, the increase in specific gravity not corresponding to the weight of oxygen absorbed. Varnishes which are inclined to skin over when stored in bulk, especially manifest a strong tendency to wrinkle on application. The formation of skins is an indication that in the case considered, the second part of the reaction :

$$A+O_2=AO_2 \qquad AO_2+A=2AO$$

indicating transference of oxygen from the surface layer to the under-portions of the film, is not complete. The fact that skinning is more often apparent in varnishes in which the oil present exists to a great degree in a polymerized form,

* R. S. Morrell, *Br. Assoc. Reports on Colloid Chemistry and its Industrial Applications*, 1920.

† *Proc. Oil and Colour Chemists' Assoc.*, 1919, II., *13*, 106–109.

‡ R. S. Morrell (*loc. cit.*).

i.e. in a form in which the stability of peroxides is at a maximum, would support this. An alternative hypothesis is advanced by H. Wolff,* who points out that the rate of oxidation in a thick film of varnish is considerably greater in the surface than in the body of the film, owing to the non-penetration of the (activating) ultra-violet rays in the latter. Thus, expansion with partial approach to a completion of the process of solidification will take place in the surface, independently of and in advance of the under layers. The fault is more pronounced in certain types of varnishes, particularly those in which solidification is influenced solely by oxidation (Co, Mn) as distinct from those favouring solidification by polymerization (Pb, Ce, etc.).† Thus, wrinkling is accentuated in varnishes which have been treated with an excess of manganese or cobalt driers.

(*f*) **"Bubbling."**—The appearance of small bubbles during application of the varnish changing subsequently to pinholes is a minor trouble, generally attributable to too rapid an application. Too low a viscosity, owing to excessive thinners, favours the formation of bubbles.

(*g*) **"Webbing" or "Crocodile-skin."**—This phenomenon is very characteristic and at first sight somewhat simulates cracks. On close examination, however, the distinction becomes apparent as a puckering-up of the surface, the excess area being taken up as ridges forming the boundaries of the "web." The fault always originates in the presence of China wood oil in the varnish, suitable treatment, however, stopping the tendency to "webbing." "Webbing" does not always manifest itself on application of the same varnish—an absence or low concentration of ultra-violet rays, together with an atmosphere highly charged with CO_2, etc., favouring its appearance. Generally speaking, it may be attributed to the presence of a large proportion of insufficiently polymerized China wood oil. Since many modern varnishes are made with China wood oil as a constituent, the liability to "webbing" should be specially tested for

* *Farben-Zeit.*, 1919, *24*, 1119.
† R. S. Morrell, *J. Chem. Soc.*, 1918, *113*, 111.

by allowing glass plates coated with the varnish to dry in an atmosphere highly charged with products of combustion.

(*h*) **Blistering and Peeling.**—Both these faults are attributable to the same cause, viz. the entrapping of ultimately volatile products underneath varnish films. In the case of blistering, solid impurities, often heavy metal soaps (driers), arising from imperfect maturing of the varnish, set up local points of decomposition of the oxidized film immediately in contact with the undercoat, with consequent development of gaseous products of decomposition which are unable to penetrate the covering film. The fault is naturally more common where the varnish film is exposed to heat. No remedy exists when once the fault occurs, but careful flatting of the undercoat is usually a safeguard against its occurrence.

Peeling is similarly less likely to occur when thorough flatting of the undercoat has been done, owing to the more perfect " key " or adhesion of the two surfaces. It is usually caused by the application of a varnish coating on an undercoat containing too much drier, for the reasons given above as to the cause of blisters forming round nuclei of drier particles.

(*i*) **" Ropiness."**—Ropiness, or the curdling of varnish under the brush, although more apparent during use, has usually occurred previous to its application. In its simplest form, it is due to chilling of the varnish with consequent disturbance of the accurately gauged viscosity and flow originally present. It must not be lost sight of that copal varnishes are at best somewhat unstable emulsoids or suspensoids very susceptible to irreversible change under extreme conditions of cold. Curdling, however, is sometimes attributable to faulty manufacture, *i.e.* incomplete " solution " of the gum-resin in the oil. It manifests itself as a gradual increase in viscosity during storage with ultimate separation of a gummy coagulum. Many varnishes are curdled by addition of raw or boiled linseed oil, petroleum spirit, other varnishes, etc.

General Flaws or Imperfections in the Surface of a

Varnish Film are often apparent to a degree out of all proportion to their cause, very small particles of falling dust, etc., causing small pips, ridges, etc. The careful straining of the varnish previous to use, employment of clean brushes, working in as far as possible a dust-free atmosphere, etc., will do much to obviate these imperfections.

Types of Varnishes

A general description of the manufacture of a typical varnish composed of gum-resin, drying oil, siccative and volatile thinner has been given in the preceding pages. It being beyond the scope of this work to enter into the composition of the many varnishes destined for special purposes, a brief description, however, of the more general types will not be amiss.

Decorator's Varnishes.—These varnishes, as their name implies, are intended for use by the house decorator, in distinction to the more exacting requirements of the coach or motor body painter. With the exception of Goldsize or Preparation Varnish already referred to, these varnishes are characterized by a fair degree of elasticity and moderate speed of drying. *Church Oak* is the term usually applied to a varnish yielding an especially hard film which does not appreciably soften at temperatures up to 40° C., it being intended for use on seats. The hardness of the film is often obtained by addition of lime to the gum-resin and oil combination, a calcium resinate of high melting-point being formed. *Mixing Varnish* is specially intended for conferring gloss to oil paints, and in consequence of the liability of the latter to contain basic pigments, should have as low an acid value as possible. *Inside Varnishes* are usually of high gum-resin content, thus giving a great degree of hardness and gloss, but not necessarily of great weather-resisting power.

Coach-builder's Varnishes.—These represent the highest art of the varnish manufacturer, and are characterized by their careful preparation, long maturing, special selection of gum-resins, treatment of oil, and nature and proportion

of driers for which the particular varnish is specially destined. It will thus be apparent that none but specially selected pale hard gum-resins and carefully treated oils would be suitable for the pale varnishes known in the trade as *French Oil, Maple* and *Venice Body Varnishes*. The terms *Body Varnish* and *Carriage Varnish* refer to their intended designations of application to the body (doors, roof), and under portion (wheels, etc.) of coaches. Japans will be dealt with below.

Varnishes for Special Purposes include such types as *Boat* and *Yacht Varnishes* (specially prepared to withstand immersion in water); *Stoving Varnishes* for the protection of metal parts where rapid application and great hardness are essential; *Polishing Varnishes* intended for decoration of articles not exposed to the weather, in which the finish is obtained by hand polishing the flatted dried film, etc.

Japans and Bituminous Varnishes

These preparations occupy a special position to themselves, since they differ in having for their characteristic ingredient a bitumen or asphalt. Both gum-resin and oil may or may not be present, as the asphaltic substances differ far more widely in their hardness and elasticity than the various gum-resins, and correction of these properties to the degree desired is thereby obtained. The most important bituminous varnish used in the higher branches of the decorative crafts is known as *Black Japan*. The method of preparation, specific choice of ingredients, etc., varies widely with the different manufacturers, so that beyond a general description of the composition and properties of this product, reference must be made for further details to the larger text-books. The specific purpose of Black Japan is in the production of a brownish-black ground of particular translucency or depth, thus differing from pigmented preparations (black enamel) which appear to reflect their depth of colour from the surface only. The main use of Black Japan in the coach-building craft is in the treatment of mudguards, etc. The varnish itself is obtained by amalgamating

specially-treated oil of great drying power with a suitable bitumen in the same way as described in the manufacture of copal varnish. The Japan itself rarely possesses a great degree of elasticity or weather-resistance, so that in use it needs to receive a coating of a suitable finishing varnish. The art of the varnish maker consists in the preparation of a Japan of a great degree of depth and intensity of colour without employing so high a proportion of bitumen that solubility of the latter in the ensuing coat takes place, a condition manifesting itself by the appearance on the finished work of an undesirable greenish fluorescence. *Brunswick Black, Air-drying Black,* and *Black Stoving Enamels* also belong to the class of Black Japans. *Black Varnish* for " patent leather " is a varnish possessing an extraordinary degree of elasticity at low temperatures combined with a high gloss and great transparency. It is obtained by suitable heat treatment of linseed oil in the presence of iron as a drier or polymerization accelerator, Prussian blue being commonly employed as the source of iron. Addition of gum-resin or asphaltum is inadmissible on account of the extreme elasticity needed.

Section II.—INSULATING VARNISHES

Owing to the high dielectric constants of resins, drying oils, and pitches, varnishes are valuable insulating materials. The following table shows the specific inductive capacity of a number of insulating materials :—

Asphaltum	2·68 (Pirani)
Plate glass	5·37–6·2 (Arons)
Paraffin	2·32–1·92 (Bergmann)
Shellac	3·1–2·7 (Gordon)
Resin	2·55 (Boltzmann)
Porcelain	4·8–6·8 (Curie)
Paper	2·0–2·5 (Pirani)
Mica	6·64–5·66 (Klemenic)
Bakelite	5·6–8·8 (Electric Test Laby., N.Y.)

The solution of resin and oil in suitable thinners permits impregnation of other insulating materials, and after volatilization of the solvent a film of non-conducting material is left with high moisture-resisting properties. In the case of many varnishes the film is sufficiently elastic to bear strain, and rise of temperature in working is often insufficient to cause brittleness so that the surface coating remains intact for long periods of time. The description of insulating varnishes is inadequate in most text-books on varnishes in English, although some firms issue brochures describing the properties and uses of their preparations. It is left to the electrical engineer to put forward his requirements and to state the conditions under which the materials are used. In this brief statement of the subject the general principles of the functions of insulating materials as laid down by Fleming and Johnson in their handbook, "Insulation and Design of Electrical Windings" (Longmans, 1913), have been closely followed. To the varnish student it will be evident

which classes of varnishes are most suitable for different systems of insulation without going into details of the composition of the mixings. To the electrician a breakdown due to defective insulation is costly and leakage of current makes economical and safe working impossible. The varnishes of insulating coatings must give maximum insulation with minimum thickness and maximum penetration combined with marked waterproofing properties.

Fleming and Johnson classify insulating varnishes as follows :—

(1) Varnishes for impregnating windings.
(2) Varnishes for treating paper and fabrics.
(3) Cementing varnishes.
(4) Finishing varnishes.

(1) **Varnishes for Impregnating Windings.**—These varnishes are used to fill the coverings of windings, thereby increasing their insulating value and rendering them moisture-resisting. They must, moreover, resist the action of the hot mineral oil which is essential for oil-immersed windings. The film should be sufficiently flexible to withstand mechanical stresses, and expansion and contraction of the windings, and retain their flexibility with age. There must be no corrosive action on copper or destruction of the fibrous insulation coverings. The varnishes should be as free as possible from organic acids which tend to become active during the process of oxidation of the varnish especially when it is stoved. This corrosive action of the organic acids is not serious except for fine windings, *i.e.* wires of 0·02 in. diameter and smaller. The corrosive action of the acids appears to cease when the varnish becomes dry. The green discoloration often noticed on windings impregnated with linseed oil resin varnishes, especially those containing turpentine, occurs during the drying process, and when once the varnish has hardened no further action seems to take place. Experience has shown that the acids in varnishes are not the main cause of insulation failures. The presence of a certain amount of mineral drier is permitted, if air-drying coatings are required, and also in stoving varnishes.

It must be pointed out that the oxidation of a varnish continues slowly even after it appears dry, so that the elasticity will gradually decrease and care must be taken in the amount of drier present and in the proportions of resin and oil present in the mixing.

An air-drying varnish is usually made to dry in 10–15 hours and a stoving varnish in 12–15 hours at a temperature of 100° C.

Pitch varnishes containing linseed oil are of more permanent flexibility, but have a lower dielectric strength and are less mineral-oil resisting.

In linseed oil varnish films only the outside is really dry.

If a resin dissolved in spirit or suitable petroleum thinner is used the windings are dry on the expulsion of the solvent, but such films lack the flexibility of linseed oil varnishes.

The shellac varnishes are suitable for insulation of low voltage windings such as instrument coils, where the temperature variation is small and there are no mechanical stresses to be considered. The coatings are, however, brittle, and although the shellac dries quickly it is not permanent in moist air.

The so-called heat-radiating varnishes are comparatively poor insulators and more satisfactory results are obtained by filling interspaces in the windings with solid compounds.

It is of the greatest importance to remove moisture from the cotton coverings before the varnish is applied, otherwise insulation may break down due to ionization caused by the water. The drying of the windings is performed preferably in a vacuum chamber, and the varnish should be allowed to impregnate the coils prior to removing them from the vacuum chamber, thereby ensuring greater penetration of the varnish. The varnishes require thinning from time to time with benzine to maintain the penetrating power, and special care should be taken to ensure that the first coat is dried before a second coat is applied. When more than one coating is applied the windings should be drained from opposite ends to ensure uniformity of coating.

Solid impregnating compounds on an asphaltum basis have now considerably superseded varnishes in the insulation of windings. The impregnation is complete in one operation, the coatings are more chemically inert and are better fillers and more moisture-resisting. A difficulty in their use is selection of the asphaltum which will impregnate the windings at a suitable temperature and will not ooze out of the windings during the working. Generally the asphaltums used soften at 105°–115° C. and do not become appreciably fluid below 150° C. If the impregnation temperature is raised too high the coverings may be carbonized and if too low the compound may ooze out when the winding is in use. These compounds are used on field coils and stationary windings, but not for revolving parts, owing to displacement by centrifugal forces, nor for transformer work, owing to rise in temperature, or for immersed types of transformers where the asphaltum may be dissolved away.

Method of Application.—The windings to be impregnated are dried in a vacuum chamber. The compound is melted in a steam-coil-heated tank and introduced into the vacuum chamber by opening a valve in the connecting pipe, the atmospheric pressure forcing the compound out of the melting tank into the vacuum chamber. The windings in the vacuum chamber are now subjected to an air pressure of 50 lbs. per square inch so as to complete the impregnation of the coils.

(2) **Varnishes for Impregnating Papers and Fabrics.**—The requirements are good flow, high moisture-resisting power, and great flexibility. It is of great importance that the physical properties of the coating materials should be permanent under working conditions. They must not be attacked by mineral acids. The presence of mineral acids is immaterial provided there is no chemical action between them and the paper or fabric. Owing to the natural moisture-absorbing powers of the paper and fabric they must be heated, but not too much, to reduce their flexibility. As in the case of all insulating varnishes a proper balance must be maintained between stoutness and penetration, and the selection of a

variety will largely depend on this factor. The thickness of the coating is about 0·002 in. A linseed oil varnish can be employed containing resin with driers, which can be stoved at 100° C. to give a smooth elastic surface with due consideration of the penetrating power and elasticity of the film.

(3) **Varnishes for Cementing Purposes.**—These varnishes are used in building up mica sheets and in the preparation of mica cloth. Spirit varnishes, shellac, or spirit soluble copal in methylated spirit may be used. These varnishes dry without oxidation and soften on heating, so that their use is restricted by temperature limitations. They are employed for the preparation of insulating tubes and for cylinders of paper and mica.

(4) **Varnishes for Finishing Purposes.**—These varnishes are used to give a smooth coating to the coils or windings which will prevent dirt or dust from accumulating on the surface. They must be air-drying and resist lubricating oil. Shellac and pitch varnishes give a smooth surface but are brittle. The varnishes may be sprayed on. Provided the windings are protected by smooth tape the impregnating varnish is sufficient, although the surface must be hand-brushed, which adds to the cost of production.

For testing the insulation power it is customary to include drying tests, breakdown voltage, the effect of hot mineral oil, brittleness, economy test (which is a test to determine the proper concentration of a varnish giving the maximum breakdown voltage), shop tests with the varnish in bulk, penetration tests whereby the depth to which a varnish has penetrated the material built up in layers, and finally the rate of moisture absorption by measuring the insulation resistances at frequent intervals of a coil immersed in water.

The testing of a varnish as carried out by the National Physical Laboratory would be on the lines of impregnating coils of double cotton-covered wire and submitting adjacent layers of the coils to an increasing alternating voltage until breakdown occurs. The pressure would be applied to the coils in steps of 100 volts for periods of 1 minute starting

at 500 volts. The varnish coating would be stoved at 155° F., 23″ vacuum or 240° F. at ordinary pressure. A good elastic insulating varnish tested under these conditions would stand an electric pressure of 1400 volts before breaking down. The coils would be dipped only once in the varnish. Doubly coated the protection would be greater. It must be pointed out that direct current breakdown voltages are always higher than alternating (about twice), probably due to less internal heating and absence of alternating dielectric stress. Generally the voltage required to produce a breakdown should be about 1000 volts per mil. in a thickness of 0·006 in.

A few figures may be quoted from Seeligman and Zieke to give some idea of the breakdown voltages, but they must not be taken as anything more, as so much depends on the thickness of the layer, the penetrating power of the varnish, and the general conditions of the tests—

Shellac (one coating)	450 volts.
Linseed oil (drying oil)	650 ,,
Stand oil	2400 ,,
Dammar in turpentine	650 ,,
Flatting varnish	400 ,,
An elastic insulating varnish ..	3000 ,,

In Part III. reference was made to the uses of Bakelite for insulating purposes. Paper impregnated with Bakelite varnish is used in the manufacture of "Micarta" sheets, "Pectinax" tubes, and transformer terminals. Paper is impregnated with the varnish and dried; and a sufficient number of the sheets of paper are then pressed together or rolled into tubes. In this way cylinders up to 3 ft. in diameter and transformer terminals from 6–9 ft. long are made to stand 100,000 volts (Williams, "Electric World," 1911).

The dielectric strength of sheets of impregnated Bakelite paper is 53,700 volts for $\frac{1}{16}$ in., compared with 50,460 volts with shellac paper. The varnishes may be used for the impregnation of coils, armatures for magnetos, arc lamps, transformers, etc. Fluid Bakelite "A" can be used for impregnation of arc lamps or magneto coils. It penetrates

through the windings and forms a solid block. It has not as yet replaced asphaltum impregnation. The coils are said, to resist mechanical shocks better than when resins are used and the heat-conducting properties, although weak, are greater than those of ordinary resinous materials. It resists acids, chlorine, and weak alkalies. It must be remembered that Bakelite requires a stoving heat of 140°–170° C., and the excessive strength of the filling renders the dismantling of the parts difficult.

In view of the varied requirements for an insulating varnish it is evident that special varnishes are wanted for different kinds of work. The risk in employment of a new kind of varnish must be great because of failure in insulation and its effects. Although much can be avoided by careful preliminary testing it must be remembered that a durability test takes time under working conditions. Thus, once a variety has been found to give satisfactory results there is little inclination to change, unless inducements are offered in the form of improved insulation, combined with cheapness of material and of application.

Section III.—SPIRIT VARNISHES

Spirit varnishes are characterized by their consisting of an alcoholic solution of resin or mixture of resins, so that the "drying" which takes place on application on a surface consists merely in an evaporation of the solvent, the resinous constituent remaining in its original state as before solution: they thus possess the advantage of drying much more rapidly than oil varnishes. Owing to the fact that a constituent which possesses the same elastic properties as the dried oil or linoxyn in an oil varnish has not yet been found, the resultant film is necessarily more brittle and never possesses the toughness which would fit it for the hard wear to which the latter class of varnishes is subjected. The properties of a spirit film varnish being intrinsically those of the particular resins chosen there is a certain variety of properties in the dried film which are limited only by the solubility of the resins. Although the individual resins possess varying degrees of toughness, a toughness approaching that of even a moderately elastic oil varnish cannot be obtained. It may be pointed out that among the spirit varnish resins may be found some which possess the properties of impermeability to gases and water, insulation, etc., which are not obtainable to the same degree in oil varnishes. Some improvements in elasticity of spirit varnish films is obtained by the addition of certain substances, which, however, at the same time seriously diminish their hardness and wearing properties. Spirit varnishes lend themselves especially to the preparation of coloured varnishes owing to the ease with which aniline colours can be dissolved in methylated spirit.

Preparation.—Of the preparation of spirit varnishes

consisting merely in the solution of the resin in alcohol little description need be given. There are three methods in general use: the first consisting merely in stirring the subdivided resin in a suitable quantity of spirit in an open vat until solution has taken place and then allowing the insoluble impurities, bark, wood, etc., to separate by settlement or filtration. The other methods purport to accelerate the solution of the resin, the most widely used being that of accomplishing solution in a horizontally-disposed wooden barrel fitted with a manhole for charging, the barrel being rotated about its horizontal axis either on geared spindles or on trunnions. The third method consists in dissolving the resin in spirit in a closed steam-jacketed digester fitted internally with stirring gear. Although the hand-stirring method of solution appears primitive it is claimed by many authorities that paler varnishes are obtained by this means owing to the lesser contact with air to which the varnish is subjected.

The further treatment of the freshly prepared spirit varnish, viz. the clearing, is either accomplished by simple sedimentation or filtration; in the latter case special precautions have to be taken owing to the volatility of the solvent. Shellac varnishes, *i.e.* alcoholic solutions of gum shellac, will only clear to a limited extent by sedimentation, a considerable amount of turbidity being present even after long standing, and filtration not being practicable owing to the fine subdivision and slimy nature of the insoluble constituent (shellac wax). This class of varnish is commonly sold and used in its turbid condition, the insoluble constituent indeed being an intrinsic and necessary part of the preparation for certain purposes ("French polishing"). The properties and uses of the spirit varnishes are best considered by reference to the individual resins which have been described in Part III. Additional facts of technical importance may be given under the following special headings of the spirit varnish resins.

Shellac.—This represents the most important constituent of spirit varnishes, possessing a degree of elasticity and

hardness distinguishing it from all other gums and resins. Shellac, as it comes into the market in its various forms of flake shellac, button lac, garnet lac, etc., is a manufactured product, the different treatments producing the lac in various forms and conditions of purity.

The preparation of shellac for the market from stick-lac embodies the separation of bark, wood, etc., removal of colouring matter, and conversion of the resin into shellac. The separated colouring matter finds an outlet on the market as lac-dye. Shellac is prepared in India by somewhat primitive methods, the first operation of separating the wood from the resin being done by crushing the stick-lac by hand, a knife being used to assist the operation of separation. The dye is removed by stirring the partly purified lac in a closed cylinder fitted with agitating gear with water or a weak solution of caustic soda, a fair proportion of the dye going into solution in the water. The water is decanted off and the dye may be precipitated with a solution of alum. The residue is then carefully dried, transferred to a roll of cotton, and the roll containing the stick-lac gradually warmed by bringing it into proximity of a fire ; the ends of the roll are twisted to squeeze the molten shellac through the cotton. The molten lac is then allowed to solidify on plates or water-cooled rolls from which it is removed in flakes of an orange-brown colour constituting the flake shellac of commerce.

Button lac is obtained in the form of large flat or slightly hollowed buttons by stirring the crude lac with hot water for several hours to remove the colouring matter, melting and casting into buttons. Adulteration of this variety with rosin is not uncommon, such admixture made partly to facilitate melting during manufacture.

Garnet lac is a special preparation of shellac characterized by being free from contained wax. The waxy constituent of shellac being insoluble in alcohol a clear solution is not obtainable from any variety but garnet lac. Shellac freed from wax is obtained by either fractionally precipitating the wax from a strong alcoholic solution of shellac by water, the wax separating out first and the shellac remaining in solution

being recovered by distillation of the alcohol, or by treating with aqueous solutions of alkali carbonate wherein the shellac dissolves, leaving the wax insoluble as a scum. In the latter method the shellac is recovered by acidification of the alkaline solution.

In connection with bleached shellac it must be pointed out that many of the specially desirable properties of the original shellac are lost, among them being the elasticity and ready solubility in alcohol. It was pointed out in a former chapter that the determination of the iodine value of shellac was a method for estimating the colophonium content, but the method is not applicable to the examination of the residue from a solution of shellac since any rosin present in the resin would become oxidized during evaporation of the solvent with consequent loss of iodine value. In such cases a quantity of shellac varnish representing about 2 grams of dry shellac is weighed into a separating funnel, 200 c.c. of petroleum ether (B.P. 35°–60° C.) added, followed by 100 c.c. water added drop by drop with shaking. This will result in the separation of two layers with an intermediate layer of shellac, the rosin remaining in the clear petroleum ether layer. The rosin can be estimated by the usual methods (McIlhiney, *J. Am. Chem. Soc.*, 1908, *30*, 867).

Of the various designations of alcoholic solutions of shellac may be cited " French polish," " patent knotting," negative varnish, bookbinders' varnish, label varnish, whilst many other varieties are obtained by suitably modifying the properties of the resin by addition of other resins, *i.e.* elemi, Venice turpentine, sandarac, etc.

The remaining resins which are used in the manufacture of spirit varnishes are entirely of vegetable origin, being solidified balsams exuding from different species of trees. These resins include Manila copal (soft variety), elemi, sandarac, etc. Of these, soft Manila copal is by far the most widely used as it enters into the composition of the pale spirit varnishes where high gloss forms a more important consideration than elasticity. The occurrence and mode of production of the resin has been described in Part III. It

appears in the market as pale yellow tears or lumps, some varieties of which agglomerate together by slight heat and pressure ("blocky gum"). The degree of solubility of different samples of Manila gum varies somewhat, many not being soluble in spirit and leaving a stringy residue. Manila resin is principally used in that variety of varnish known as "white hard spirit varnish."

Manila varnishes are also considerably used as vehicles in the manufacture of spirit paints and enamels. Addition of small percentages of castor oil or linseed oil fatty acids is often made to reduce the brittleness of the dry film of resin. Sandarac, as one of the hardest of the spirit soluble gums, is employed as an addition to spirit varnishes to impart hardness to the film. Its brittleness precludes its extended use as the sole constituent of a spirit varnish.

Benzoin, often erroneously termed "gum Benjamin," is the product of *Benzoin officinale* (cf. Part III.). It is relatively unimportant, being used by the varnish maker mostly on account of its characteristic odour. The alcoholic solution of gum benzoin appears in the Pharmacopœia as tincture of benzoin or Friar's Balsam. Benzoin finds its principal application as an addition to spirit varnishes in small proportion, its aromatic odour rendering it useful in improving the odour of spirit varnishes intended as leather dressings.

Acroides Spirit Varnishes.—The red acaroid resin is used only for coloured spirit varnishes. It is strongly light absorbing, and a concentrated solution containing a little castor oil or copaiba balsam gives a red-coloured film which may be used to coat the windows of photographic laboratories so as to exclude actinic rays.

It is often mixed with shellac spirit varnishes and used as shellac substitute as it dries quickly and hard. In North America the red resin is used in large quantities in leather making. Its special important property of holding, even in spirit solution, small quantities of rubber enables it to furnish elastic films which are stated to be water-resisting. It is used in sealing wax and for making aromatic

soaps. Attempts to bleach the resin have not been successful and the strong colour of both varieties limits their use except for " knotting." The high percentage of insoluble matter makes purification advisable before it can compete successfully with other spirit soluble resins.

Section IV.—CELLULOSE ESTER VARNISHES

Although solutions of cellulose nitrate have been known and used for a number of years, the particular properties shown by films consisting of cellulose acetate tempered by various plasticizing agents have brought these products to the forefront during the War.

The cellulose nitrate (erroneously referred to as nitrocellulose) varnishes have for their commonest representatives the well-known collodions and celluloid.

The collodion of the British Pharmacopœia consists of pyroxylin or cellulose nitrate $C_{18}H_{21}O_6(OH)(NO_3)_8$, dissolved in a mixture of three parts of ether and one of alcohol.* The resulting emulsoid appears as a viscous translucent colourless liquid. On evaporation it leaves a harsh brittle film which often dries porous and opaque, owing to the presence of water deposited within the film and originating from condensed moisture from the surrounding air, the latent heat of evaporation of the volatile ether solvent causing considerable lowering of temperature. The brittleness of collodion is modified by addition of castor oil and Canada balsam in flexible collodion or collodion flexile (B.P.). The high rate of evaporation, inflammability, and tendency to dry to an opaque film are modified in commercial forms of cellulose nitrate solutions by replacing the ether-alcohol by amyl acetate with addition of castor oil to impart flexibility to the film. Lower nitrates of cellulose down to the dinitrocellulose are also employed as a basis of the cellulose nitrate varnishes in combination with other solvents and non-solvents, *e.g.* acetone, methylated spirit, benzol, and petrol, etc.

* Cellulose trinitrate (gun cotton) is insoluble in a mixture of ether and alcohol.

A solution of nitrated cotton in the above-mentioned solvents is known as "Zapon," a colourless lacquer for protection of bright metal parts from rusting and tarnishing. As an adhesive it is often blended with shellac to give a lustrous coating for metals.

Celluloid Varnishes.—If collodion wool is mixed with camphor and heated under pressure it is transformed into celluloid. Celluloid requires the same solvents as collodion, giving a varnish which is colourless, lustrous, and adherent, which does not crack and may be easily coloured like all spirit varnishes by solutions of aniline dyes. The addition of castor oil renders the coating more elastic and more adherent. They are tougher than collodion varnishes and may be applied in thicker coats, *e.g.* up to $\frac{1}{8}$ in. thick, and the coats are brilliant and adherent, waterproof but highly inflammable.

Cellulose Acetate Varnishes.—It is safe to assume that the great importance which the manufacture of this product has assumed has been entirely due to the part which cellulose acetate varnishes ("dopes") have played in the War. Cellulose acetate films have the distinctive property of possessing relative uninflammability, in addition to which those obtained from cellulose acetate, prepared under certain specific conditions, when applied to linen fabric have the property of inducing increased tautness. The importance of this latter property will be recognized when considered from the standpoint of application to a stretched fabric, viz. the wings of aeroplanes. The "solubility" of cellulose acetates in different media is dependent on the mode of preparation of the ester just as in the case of the cellulose nitrates, but the variety chosen for the preparation of aircraft dopes is not dissolved in the usual nitrocellulose "solvents," acetone and its homologues with other "solvents" and "non-solvents" being usually employed.

In the manufacture of dopes, "plasticizing" agents, *e.g.* triphenyl phosphate, etc., are added to reduce the brittleness of the film whilst retardation of the rate of evaporation of the volatile continuous phase is effected by addition of

certain liquids of high boiling point, viz. benzyl alcohol, terpineol, etc.

The lower degree of inflammability of cellulose acetate has not resulted in the adoption as a base for varnishes other than those intended for covering aircraft wings owing to its higher cost and the relative unimportance of the inflammability.

Cellulose acetate sols, on the basis of a different variety of ester to that used in dopes, are used in the manufacture of artificial silk fibres. It must be mentioned that in consequence of the high viscosity simultaneous with low concentration of the sols of both cellulose nitrate and acetate their employment in place of either copal or spirit varnishes is hardly likely to take place when the question of the necessity of application of films of tolerable thickness comes into question. For outside wear the dope is sensitive to the actions of ultraviolet rays and must be protected by incorporation with a protective pigment, moreover its water-resisting power is not very great and it has to be covered with a varnish of low water-absorbing power, preferably a China wood oil varnish. (For an account of the commercial development of the manufacture of cellulose acetate, see E. C. Worden, *J. S. C. I.*, 1919, *38*, 389.)

Section V.—ANALYSIS OF VARNISHES

The usual varnish examination includes the determination of specific gravity, flash point, colour, viscosity, the amount and nature of the solvent or thinning spirit, a qualitative test for rosin, and the gravimetric estimation of the ash yielded on ignition of the varnish. Moreover, a drying test on glass or on a prepared wood panel and examination of the rubbing properties as well as the action of hot and cold water on the film are noted. It is evident that the above tests give inadequate information as to the durability of the coating which can only be satisfactorily determined by several months' exposure. To a very limited degree the expert can predict the properties of a varnish film, but the dependence of the properties on composition is by no means certain, owing to the difficulty in estimating the proportions of resin and oil in any mixing as well as the lack of knowledge of the connection of the properties of the fused resins with their physical and chemical constants. The separation and determination of the thinner is comparatively easy and accurate (de Waele and Smith, *Analyst*, 1918, *43*, 408). The separation of the resin and oil is difficult and the identification of the components is by no means certain. The different processes employed for the depolymerization of the gum introduce difficulties in the identification of the separated resins. At present there is no agreement as to the estimation of the component oils which may be present in a more or less polymerized state. The changes which occur in the "ageing" process undoubtedly modify the properties of resin and oil. A summary of the methods employed in varnish examination is given by Boughton

(Technological Papers of the Bureau of Standards, No. 65 : "Determination of Oil and Resin in Varnishes," Washington, 1916). It is evident that if the estimation of the glyceryl radicle in an oil mixing were accurate the determination of the oil would be easy, although no distinction could be drawn between simple and polymerized oil. It must be pointed out that the saponification value of a varnish is useless, because the resins contain esters. Attempts to separate the resin from the oil by use of special solvents has not met with success. Vorhees (*Bull.* 109, Bureau of Chemistry, Dept. of Agr., U.S.A.) proposes to separate resins by petroleum ether, which dissolves the oil and part of the resins, and transforming the oils into linoxyn by oxidation. Treatment with chloroform will separate the resin from the insoluble linoxyn. Boughton considers the method inaccurate for general use. The separation of resins and oils has been attempted by an esterification method depending on the more rapid esterification of the oil acids in the presence of resin acids. This method was suggested by Twitchell (*J. Soc. Chem. Ind.*, 1891, *10*, 884), and has been criticized and modified by many workers (Gill, *J. Amer. Chem. Soc.*, 1906, *28*, 1723 ; Holley, "Analysis of Paint and Varnish Products," 1912, 259 ; Lewkowitsch, "Oils, Fats, and Waxes," 5th Edition, III, 165 (1915) ; Boughton, *loc. cit.*).

In the opinion of one of the writers the difficulty lies in the proper control of the rate of esterification of the oil and resin acids as will be evident from the description of the process : after the removal of the thinners the resins and oils are saponified and the unsaponifiable matter is collected and taken as part of the resin. The soap solution is treated with acid and the liberated fatty and resin acids are esterified in absolute alcohol solution by gaseous hydrochloric acid whereby the former are transformed into ethyl esters and the latter are considered to be unattacked. The mixture of oil esters and resin acids is treated with petroleum ether and shaken with dilute aqueous potassium hydrate which extracts the resin acids. The petroleum ether contains the oil esters which are weighed directly. From the aqueous

alkaline solution addition of acid liberates the free acids, which can be collected and weighed as resin together with any solid matter which is insoluble in petroleum ether. If the esterification has been incomplete the resin values will be high owing to contaminated oil, whereas if it has been carried too far the oil content will be too high owing to the presence of resin esters. The method works fairly satisfactorily if rosin and linseed oil are alone present, but with copal resins, polymerized oil or China wood oil mixings the method is not so reliable. The following figures obtained by one of the writers will give a rough idea of the degree of accuracy of the method if the esterification is carefully controlled :—

	Found.*	Calc.	Found.*	Calc.
Turpentine ..	41·36	41·3	40·45	43·5
Oil (linseed) ..	38·77	34·81	42·29	40·52
Resin	13·8	14·0	14·77	14·9
Residue (driers) ..	3·07	1·89	0·83	1·34

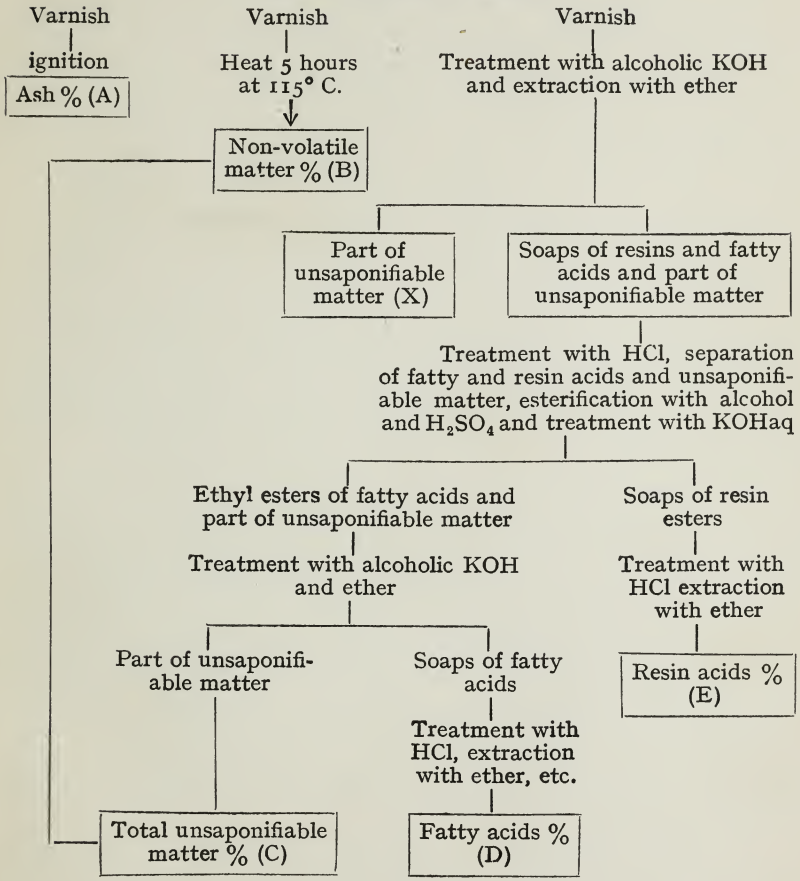
McIlheney (*Proc. Am. Soc. for Test. Mat.*, 1908, *8*, 596) has modified the method, but Darner (*N. Dak. Agr. Exp. Sta. Paint Bulletin*, 1915, 1, No. 6) and Boughton (*loc cit.*) find that the modification is unsatisfactory when tung oil is present and the separation of the precipitated resin is very troublesome. The results obtained by one of the authors is in agreement with Darner and Boughton (see p. 225), and he is of the opinion that the substitution of methylated ether for petroleum ether by Boughton, although preventing emulsions and shortening the method, introduces an error owing to the partial solubility of the resin acid salt in methyl ether, but he agrees with Boughton that methods involving esterification by Twitchell or Wolff Methods (*Chem. Zeit.*, 1914, *38*, 369) are the best so far devised for practical use, although the accuracy leaves much to be desired. The method is tedious, and to obtain satisfactory results large quantities of varnish (60 grams) ought to be used.

An attempt to estimate the amount of polymerized oil was made by treating the resin and oil after

* Mean of 3 analyses.

	McIlheney's method.	Twitchell method.	Calc.
Resin	20·5	17·0	15·0
Oil (linseed and tung oil)	31·28	34·5–36·4	35·87

Scheme of Boughton's Method.


Varnish
ignition
Ash % (A)
Varnish
Heat 5 hours at 115° C.
Non-volatile matter % (B)
Varnish
Treatment with alcoholic KOH and extraction with ether
Part of unsaponifiable matter (X)
Soaps of resins and fatty acids and part of unsaponifiable matter
Treatment with HCl, separation of fatty and resin acids and unsaponifiable matter, esterification with alcohol and H_2SO_4 and treatment with KOHaq
Ethyl esters of fatty acids and part of unsaponifiable matter
Soaps of resin esters
Treatment with alcoholic KOH and ether
Treatment with HCl extraction with ether
Part of unsaponifiable matter
Soaps of fatty acids
Resin acids % (E)
Treatment with HCl, extraction with ether, etc.
Total unsaponifiable matter % (C)
Fatty acids % (D)

D = Oil %.

B − (A + D) = Resin %.

Products marked X may be disregarded unless it is desired to check the percentage of resin as follows:

$$(C + E) \times 1{\cdot}07 = \text{Resin (\%)}.$$

removal of the thinners with acetone (Morrell, *J. S. C. I.*, *34*, 1915), and the soluble and insoluble portions were estimated separately for gum and oil content. For example, in the analysis on p. 224, the ratio of thick to thin linseed

oil was found to be 1 : 2·5, a ratio quite different to the calculated amount of thick oil present, but explicable by the polymerization occurring during making and "ageing" of the varnish.

The identification of the resins and oils is difficult, and it is evident that the resins and oils separated in the analysis will not be very closely connected in their constants with those of its components. For example, referring to analysis already quoted :

	Original oil.	Oil separated.	Resin separated.	Original resin.
Iodine value	185	92–106	85·7	109
Saponification value ..	190	172–186	101–110	120–130
Acid value	1–2	1·4	27	22–28

The presence of polymerized oil accounts for the reduction in the iodine value as well as absorption of HCl during the Twitchell esterification. Nevertheless some deductions may be drawn as to distinction between soft Manilla and Congo copals.

The great difficulty in the estimation of a varnish lies in the necessity of using large quantities of material and the tediousness of the separation. In fact, the analysis of a varnish constitutes a research which makes it difficult to obtain results in reasonable time for practical purposes. There is great need for a rapid and accurate method of examination. For the estimation of metallic driers the ignition of the varnish and estimation of the metallic oxides by the usual gravimetric or volumetric methods is quite straightforward.

A. de Waele (*Proc. Oil and Colour Chemists' Assoc.*, 1920, *17*, 75) draws attention to the necessity of interpretation by a varnish technologist of the results obtained by analysis, and on a basis of consideration of the technology of the varnish-making process gives a method of which the following is a resumé. The method is somewhat involved in manipulative detail, and the reader is referred to the original paper.

The volatile thinner is estimated by a simplified method of distillation with water (A. de Waele and F. Smith, *Analyst*,

1917, *42*, 170, and A. de Waele, *Analyst*, 1918, *43*, 408), two to three grams of varnish only being used for the determination, and the residue of fixed oils, resin, and drier being employed for the remainder of the analysis. The non-volatile residue is saponified with strong potassium hydroxide in benzol-alcohol, the soap evaporated to dryness, taken up with water, acidified under ether, and the aqueous layer, consisting of the mineral matter present as drier, etc., separated off and discarded. The acid ethereal layer is then shaken up with excess of potash and the unsaponifiable matter remaining in the ethereal layer estimated in the usual way. The intermediate step of acidification of the soap solution with subsequent reconversion into soap has for its object the removal of lead, calcium, etc., which might be present from rosinate and which would subsequently interfere with convenient separation.

The soap freed from unsaponifiable matter is then acidified under petroleum-ether (b.p. 35°–60° C.), whereby "gum-resin acids" separate as a flocculent intermediate layer. These are removed, dissolved in ether, and weighed. The petroleum-ether layer, consisting of resin acids from both rosin and gum-resin together with fatty acids from the oil are then evaporated to dryness and esterified in 95 per cent. alcohol with 1 c.c. of strong hydrochloric acid as catalyst for 30 minutes at boiling temperature. An equal volume of petroleum-ether is added, the acid present neutralized with normal alkali, and water added to an amount sufficient to dilute the alcohol present to 60 per cent. strength. This ensures adequate separation of the alcohol and petroleum-ether layers whilst inhibiting hydrolysis of the rosin soap. The aqueous layer is then separated, the petroleum-ether layer re-extracted with water once or twice and the extracts united. The aqueous extract is finally acidified under ether, which latter will then contain the resin acids from rosin and part of the gum-resin.

For the calculation of analytical results, the original paper must be consulted, as the author makes provision for the cases of differently constituted varnishes. In brief,

however, the gum-resin present is obtained from the unsaponifiable matter (less a deduction for unsaponifiable matter from the oil present), together with the gum-resin acids, a factor being employed on account of undeterminable fraction lost as water soluble, etc. Rosin is obtained from the unsaponifiable matter and resin acids, the allocation of these two fractions to rosin being determined by special considerations of composition.

By a series of tests on the petroleum-ether insoluble layer the author differentiates between "true gum acids," oxidized fatty acids, and oxyabietic acid from rosin. By the recognition of a fraction of the rosin occurring as petroleum-ether insoluble, the author probably accounts and corrects for the low figures obtained for rosin in McIlheney's method (*Proc. Amer. Soc. for Test. Mat., 8,* 596).

The method of analysis is supplemented by a series of physical tests, amongst which it is interesting to note that the author differentiates between *physical* and *chemical* "weather resistance." Physical weather resistance is referred to as the provision of adequate elasticity and hardness under the particular conditions of exposure of the product, and is thus dependent on ratio of resin to oil, whilst chemical weather resistance is determined by the stability of the oil component to atmospheric oxidation beyond that limit which marks the maximum increase in weight on oxidation (see p. 41). For the determination of the latter, the author allows "20 volume" hydrogen peroxide to evaporate on the dried film of varnish, and notes the relative corrosions effected by this reagent. The paper embodies also standardized procedures for determining resistance to water ("chalking"), etc., and includes suggested specifications for various classes of varnishes.

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